

# METALLURGIA

*The British Journal of Metals*

(INCORPORATING THE METALLURGICAL ENGINEER)

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**EXTRUDED RODS & SECTIONS**

# METALLURGIA

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## Production Changes

In an earlier issue we commented on the fact that in certain works production was easing down, and this had caused a general impression that the need for increased production had ceased to apply. We endeavoured to show that this impression was wholly wrong, because it must be obvious that attacking forces not only need more armament and equipment, but they consume more than forces entirely on defence. One aspect of the production problem especially mentioned as likely to be responsible for easing up in the production of certain types of munitions was the changing needs of the Forces due to the changing character of the various battle fronts. It was suggested that these changes would be better understood if an authoritative representative of the Ministry of Production explained the position, when a change in production became necessary, so that there would be less cause for the feeling arising that production was slackening.

The position was recently reviewed by the Minister of Production, Mr. Oliver Lyttelton, in which he referred to the war situation at the beginning of this year, the outstanding feature of which was the fact that we had for the first time succeeded in securing the strategical initiative; while on the production front we had reached a position where, having largely built up the "Capital equipment" of the Armed Forces, especially of the Army, we were in a position to adopt a selective policy of concentrating our production upon those weapons and items of equipment which could bring the maximum impact upon the enemy.

Recent events reinforce and expand the trends then foreseen and emphasise that we must swing over more and more of our resources to meet the growing opportunities of heavier and concentrated attacks upon the enemy. A good deal of hard work and careful planning has been involved in changing the production programme to meet the new conditions, and in further and more extensive changes still to come. As soon as it is decided, that any particular type of production is to be reduced a survey is made of the various firms making the equipment in question and detailed decision taken regarding the distribution of the cut over these firms, after examining the labour demands in the various areas and the possibility of reusing firms for alternative work. Until now it has been possible to plan the change so that the heaviest cuts have fallen on those areas where there were already large unsatisfied demands for additional labour. In this way the labour released from work for Army supplies has, in nearly every case,

been rapidly reabsorbed on aircraft or naval work. These changes cannot be made without experiencing difficulties; they involve inconveniences and disturbances that give cause for complaints, since it means that workers may be required to change from the production of some component on which they are skilled to another on which some training is necessary before they are efficient enough to suffer no loss in earnings. It may, and frequently does, mean moving to another firm. But these inconveniences and disturbances, incidental to changes, are inseparable from industry and are a normal experience of peace-time activities; they have long been accepted by both managements and workers. Under present conditions, despite occasional grousing, there is every indication that the changes are being taken in the right spirit, and everyone is co-operating to give effect to them.

The problems associated with production changes tend to become more difficult as the war proceeds. Apart from the stringency of man-power, strategy demands that we stop or reduce the production of weapons and equipment which have either become obsolete, were specially needed for desert warfare, or of which abundant supplies are available. It is only by this means that we can concentrate our productive energies and resources upon those weapons of the most modern type which battle experience has shown to possess the maximum offensive qualities.

Foremost amongst such weapons is aircraft. Unlike many other types of munitions, aircraft is a wasting asset with a very high obsolescence rate. This is due not only to the actual losses sustained in operations, but also to the constant need to maintain superiority of performance. The great increase in air offensive is directly related to the output of aircraft, and further increases in this offensive will be possible only to the extent that our production can be stepped up. To give effect to this, a further expansion in aircraft is planned.

Further increases in certain types of naval vessels are also planned, and in the numerous scientific instruments and other devices used in war at sea. In the highly technical field of radio equipment we were well ahead of Germany at the beginning of the war, but it is only by intensive development that we have maintained our lead. The need of this equipment is greatly increased. Thus, production changes must be accelerated, but over all the plans provide for still further increases in total production, and we must see to it that these higher targets are achieved.

The fact that goods made of raw materials in short supply owing to war conditions are advertised in "Metallurgia" should not be taken as an indication that they are necessarily available for export.

## Metallurgical Institutes

THE various technical institutes are playing a very useful part in the country's emergency. In the early days of the war it was thought that war conditions would make the usefulness of these institutes almost negligible, actually, however, they have had a stimulating effect, and all the institutes that are concerned with metallurgy are more active to-day than at any time in their history. The main purposes of each of the institutes in this category are to provide a means of communicating matters bearing upon the manufacture of ferrous and non-ferrous metals and alloys and for the arrangement of meetings to discuss practical and scientific subjects concerned with the manufacture and working of these metals and alloys.

It is true that the meetings, which are so valuable in maintaining contact between members, have been drastically curtailed. But even these show a tendency to increase rather than to diminish, and although general meetings have only been attended by a small fraction of members in comparison with peace-time meetings, local meetings continued to function on definite programmes, even during the most difficult times. Difficulties of transport and rationing, and the need for greater concentration of each member on emergency work, have reduced the time afforded for the larger general meetings, but vitally important work is being performed by these institutes in disseminating information that has a direct effect on production, both qualitative and quantitative.

Elsewhere in this issue is published parts of some of the more recent work of the Iron and Steel Institute and the Institute of Metals. In the main, long-range researches have been discontinued; this has been due largely to the need for the solution of more immediate new problems, but experience has shown that the solution of certain problems, which have an important bearing on production, can only be reached by a fuller understanding of fundamental questions.

Much of the work done by these institutes, since the war began, cannot yet be made public. The publication of papers has been hindered somewhat by the need for secrecy: however, a great number of extremely important and immediately useful papers are being published regularly. Actually, these institutes are as active as, if not more than, before the war. They are doing admirable work in meeting the need for the latest scientific and practical information on metals and alloys to forward the war effort and at the same time active work is proceeding on post-war problems, associated in some measure with substitutes, which have had to be employed under war conditions, with a view to stimulating the use and scope of the various metals and alloys in peace-time reconstruction. When a full report of the war-time activities of the technical institutes becomes available it will be found that each has made a valuable contribution.

In addition to the normal work of these institutes, an important feature of the service they are giving to members is the information they have been able to gather regarding enemy literature on ferrous and non-ferrous metals. This work has presented many difficulties and the various organisations are to be congratulated on their successful efforts to keep members in touch with developments.

## Outworking

IN the early part of the nineteenth century outworking was in fairly common operation in many European countries, including this country, but with the introduction of workshops and factories, designed to bring together increasing numbers of operatives and to make use of machinery, this system of working ceased to have any appreciable importance. During the last two years, however, the system has returned, and the latest figures show that 20,000 out-workers are now engaged in Britain at the present time.

There is no doubt that the most efficient place to manufacture goods is in a factory, but the strain on the nation's labour resources necessitates many expedients that would not be justified under normal conditions. In some localities labour demands exceed supplies, and imported labour tends to increase the strain on resources; it can be relieved to some degree, however, by taking from congested areas any portion of the work done there which can, by the exercise of a little ingenuity and trouble, be carried out elsewhere, thus providing a means of harnessing the productive capacity of workers who cannot, for various reasons, leave their localities.

The Ministry of Production, in collaboration with the Ministry of Labour and the Supply Departments, has recently issued a brochure describing several different types of outworking schemes throughout the country and explaining how to organise such schemes. The attention of managements is especially directed to these schemes in whose areas additional labour is still required to meet expanding production programmes, and where outworking is likely to provide a means of meeting part of the requirements.

Outworking falls into two main categories; for instance, arrangements can be made for people to do work individually in their own homes, in small groups working in the homes of their friends, or in suitable rooms in the locality; on the other hand, halls or other premises in suitable centres may be taken over and opened up as a small branch works to be manned by local people operating on a spare-time basis.

The problem is not to find outworkers, but to convince manufacturers of the advantages of outwork in areas where demands for additional labour for the expanding production programmes are still unsatisfied. Apparently, more people are prepared to do outworking than there is outwork for them to do. A great deal can, however, still be done, and industrial managements in congested and industrial towns are asked to examine all the jobs now being done inside their factories and study how they can make better use of labour available. Interested manufacturers should make arrangements in consultation with the officers of the Regional Boards, with whom they normally deal, so as to avoid unnecessary duplication in the same non-industrial or rural district. Regional Controllers of the Ministry of Production have undertaken to act as the co-ordinating authorities for the establishment of outworking schemes.

The brochure gives some interesting examples of successful outworking schemes. There is the case of an electrical firm, for instance, which discovered that 116 jobs were capable of being outworked. Three firms were willing to become agents, and these distributed work to the surrounding district. A staff was provided to give instruction, and in less than 24 hours of delivery of the first load an urgent request was received for more.

# On the Solubility of Silver in Mercury

By Douglas Rennie Hudson B.Sc., Ph.D.

(Lecturer in Metallurgy, Heriot-Watt College, Edinburgh).

## ABSTRACT.

From determinations of solubility of silver in mercury carried out in sealed glass bulbs, together with liquidus data, it is shown that solubility right up to the melting-point of silver can be represented very closely by three straight lines:—

$$\log_{10} N_{Ag} = 0.67035 - 1134.7 T^{-1} \quad \text{up to } 330^\circ \text{ C.}$$

$$\log_{10} N_{Ag} = 2.9065 - 2481.8 T^{-1} \quad 330^\circ \text{ to } 450^\circ \text{ C.}$$

$$\log_{10} N_{Ag} = 0.7441 - 918.2 T^{-1} \quad 450^\circ \text{ up to m.pt. of silver}$$

Their intersections, however, have no relation to the peritectic formation temperatures of  $Ag_5 Hg_4$  at  $276^\circ \text{ C.}$  and  $Ag_5 Hg_8$  at  $127^\circ \text{ C.}$ , and these points do not appear at all on the plot of  $\log N_{Ag}$  against  $T^{-1}$ , which according to Schröder's equation  $\log N_1 = \frac{H_f}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)$  should be a single straight line. At ordinary temperatures the solubility is only about a fortieth of that given by this equation derived thermodynamically, or about a hundredth if  $H_f$ , the latent heat of fusion, is corrected for temperature variation.

The approximate expression applicable to unlike atoms  $RT \log_{10} N_{Ag} = KN^2_{Hg} = K(1 - N_{Ag})$  fits observed values very well up to the boiling point of mercury, if  $K = 465$  as calculated from the experimental value of solubility at the steam-point; even beyond the limit of agreement it yields an analogous reversed  $-S$  curve. A roughly parallel curve holds for silver dissolved in liquid tin. In Hildebrand's more exact equation (in which  $a$  is the "ideal" solubility given by Schröder's equation)—

$$RT \log_{10} \left( \frac{a_1}{N_1} \right) = V_1 \left( \frac{N_2 V_2}{N_2 V_2 + N_1 V_1} \right)^2 \left[ P_1^{\frac{1}{2}} - P_2^{\frac{1}{2}} \right]^2$$

the observed solubility leads to a value of 14 for  $[P_1^{\frac{1}{2}} - P_2^{\frac{1}{2}}]$  compared with approximate values of 24, 41, 15, 18, 39, calculated from very different purely *physical* properties. The deviation from Schröder's straight line deduced from Raoult's law is therefore only a half or third of that which might be calculated from the internal pressure  $P$  of the two metals as indicated by known data. It is concluded that the mutual attraction within a pair of unlike atoms  $Ag-Hg$ , is in this case greater than the geometric mean of those within pairs of like atoms,  $Hg-Hg$  and  $Ag-Ag$ . This is in sharp contrast to the behaviour of most organic molecule pairs hitherto investigated, and to previous conjectures. It is, however, concordant with the existence of two intermetallic compounds of silver and mercury, relatively stable, and existing in well-defined space lattices.

**N**UMEROUS determinations of the solubility of silver in mercury have been made at isolated temperatures, as well as over short ranges; chief among the latter are the careful and very concordant determinations emanating from Sunier's laboratory.<sup>1, 2, 3, 4</sup> Above  $200^\circ \text{ C.}$ , however, about which trouble due to vaporisation becomes acute, one value only—that of Reed at  $212.7^\circ$ <sup>4</sup>—is available.

By carrying out the determination within a sealed tube of refractory glass it has been found possible to attain a temperature as high as  $450^\circ \text{ C.}$ , substantially above the boiling point of mercury at normal pressure at  $356.7^\circ \text{ C.}$  The effect of the increase of external pressure due to the enhanced vapour pressure of mercury will be at least of the same order as that on the melting point of silver. By the Clausius Clapeyron equation—

$$\frac{dT}{dP} = \frac{T(V_2 - V_1)}{H_f}$$

this may be calculated for the experimental conditions to be a few thousandths of a degree per atmosphere, or a little over  $0.02^\circ \text{ C.}$  at  $450^\circ \text{ C.}$  This is quite negligible

compared with the thermostatic error when boiling liquids are used.

Up to  $330^\circ \text{ C.}$  solubility follows accurately the simple exponential law, but there a sharp break occurs. In the lower ranges the present results confirm established values, and in the higher range they dovetail very accurately into Murphy's thermally determined liquidus points.<sup>18</sup> From consideration of all data available, solubility can be expressed very closely right up to the melting point of silver by three straight lines:—

$$\log_{10} N = 0.67035 - 1134.7 T^{-1} \quad \text{up to } 330^\circ \text{ C.}$$

$$\log_{10} N = 2.9065 - 2481.8 T^{-1} \quad 330^\circ \text{ C. to } 450^\circ \text{ C.}$$

$$\log_{10} N = 0.7441 - 918.2 T^{-1} \quad 450^\circ \text{ C. to melting point of silver.}$$

It is reasonable to correlate their intersections at  $330^\circ$  and  $450^\circ$  with the peritectic formation temperatures of  $Ag_5 Hg_4$  at  $276^\circ$  and  $Ag_5 Hg_8$  at  $127^\circ$ , but a careful large-scale plot of all results showed that this definitely would not hold. Despite their constant formation temperatures and measurable heats of formation, these phases do not manifest themselves in any sense on the logarithmic plot, and below  $330^\circ \text{ C.}$  this departs from a straight line only by a slight and consistent concavity. The slopes of the upper and lower branches are approximately equal, while that of the middle portion is much

<sup>1</sup> Sunier and Hess, *J. Amer. Chem. Soc.*, **50**, p. 662, 1928.

<sup>2</sup> De Right, *J. Phys. Chem.*, **37**, p. 405, 1933.

<sup>3</sup> Maurer, *J. Phys. Chem.*, **43**, p. 515, 1938.

<sup>4</sup> Reed, *J. Amer. Chem. Soc.*, **50**, p. 662, 1928.

greater, on this basis solutions up to  $N_{Ag} = 0.06$  and  $N_{Hg} = 0.7$  may be regarded as "dilute" even though deviating greatly from Raoult's law.

Schröder's elementary equation for solubility is well known<sup>5</sup>—

$$\log_e N = \frac{H}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)$$

In this  $H$  is the latent heat of solution, approximately equal to that of fusion. The expression implies that solubility is independent of the solute, provided Raoult's law holds. We denote this "ideal" solubility by  $a$ . The derivation assumes tacitly that the components do not vary except in label (or at least not very greatly)—i.e., properties like polarity, constitution, volume, are almost identical. In polarity silver and mercury are almost identical, standard electrode potentials being 0.799 V for  $Ag/Ag^+$  and 0.798 V for  $Hg/Hg_2$ . In atomic structure they are not dissimilar.

Atom.	K	L	M	N	O	P	Term Symbol.	Atomic Mass.
	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d	6s 6p 6d		
Ag No. 47 .....	2	2 2	2 6 10	2 6 10	—	—	$^2S_{1/2}$	107.88
Hg No. 80 .....	2	2 2	2 6 10	2 6 10 14	2 6 10	2	$^1S_0$	200.61

Both atoms possess 2 : 6 : 10 orbitals (at 4s : 4p : 4d and 5s : 5p : 5d levels respectively), which one would expect to be roughly equivalent in screening the nucleus, the Ag atom in the N shell and the Hg atom in the O shell; the latter atom has two "free" electrons compared with one in the silver atom. These outer electrons have always been regarded as determining the valency of an element in "chemical" combination (octet bonding), but in intermetallic combination they are probably less important than electron : atom ratios. For example, the very unusual ratio of 21 : 13 which holds for the complex brass structure has been explained beautifully by Jones<sup>6</sup> on the basis of Brillouin zone filling. The massive atomic volumes of silver and mercury, extrapolated where necessary, are 10.81 and 14.80 (liquid), 10.27 and 14.27 (solid). The pseudo lattice structure of liquid mercury, possibly cybotactic, is to a first approximation a close-packed lattice structure identical with that of silver ( $a = 4.077\text{\AA}$ ); that of solid mercury is a simple rhombohedral lattice with  $a = 3.00\text{\AA}$ ,  $\cos \alpha = 1/3$ ,  $\alpha = 70\frac{1}{2}^\circ$ , this may be regarded quite accurately as a face-centred cubic lattice distorted by a shear stress along and parallel to one face. The nearest distance of approach between atoms is thus 2.833 $\text{\AA}$  and 3.00 $\text{\AA}$  for silver and mercury respectively. Thus the present pair shows a definite but not extreme difference, instead of the identity or near-identity postulated in the thermodynamic derivation.

Attempts to forecast deviations from ideality have been made by the basis of (a) cohesive energy density by Scatchard,<sup>7</sup> (b) pseudo-cubic lattice structure in the liquid solution by Heitler,<sup>8</sup> (c) van der Waals' forces by Van Laar,<sup>9</sup> (d) statistical mechanics by Guggenheim,<sup>10</sup> and by Rushbrooke,<sup>11, 12</sup> Using probability functions and assuming (1) negligible repulsion, (2) spherical symmetry, (3) attraction between unlike molecules to

be the geometric mean of those between like molecules, Hildebrand<sup>12</sup> has derived the equation which has been confirmed by Butler<sup>13</sup> using Langmuir's treatment—

$$RT \log_e \left( \frac{a_1}{N_1} \right) = V_1 N_2 \left[ P_1^2 - P_2^2 \right]^2$$

in which  $P$  is the internal pressure. For dilute solutions (i.e., at both ends of the system) this reduces to the simple form—

$$\log_{10} \left( \frac{a_1}{N_1} \right) = \log_{10} \gamma = \frac{k (1 - N_1)^2}{T}$$

which can be used as an approximation over the whole range if  $V_1$  and  $V_2$  are not too different. When  $V_1 = V_2$  it holds for all values of  $N$  between zero and unity. This equation gives a plot of  $N$  against  $T^{-1}$  as an elongated reversed-S. This is well shown in Fig. 1, with the theoretical solubilities of iodine in ethylene dibromide, carbon disulphide, chloroform, and carbon tetrachloride,

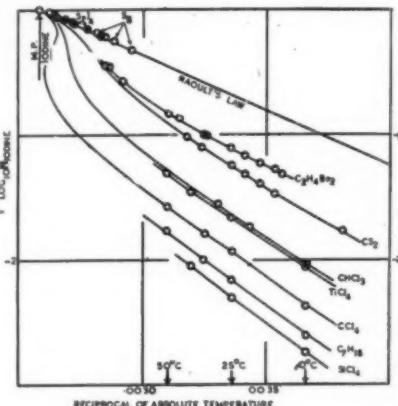


Fig. 1.—Logarithmic solubility of iodine in organic and inorganic solvents, showing degradation from the ideal as the difference in internal pressures increases.

with diminishing values of  $k$ . Most of the solubility data hitherto available are spread over too short a range of temperature to demonstrate this unexpected shape. An interval exceeding 50° C. is uncommon, while in the present work it exceeds 950° C., allowing the shape of the curve to be explored much more accurately. The experimental data for the solubility of silver in mercury give a plot strikingly similar to the theoretical curve for iodine in chloroform calculated wholly on data relating to one physical property—the latent heat of vaporisation—and entirely without reference to chemical combination or solvation. Calculation of  $N$  as a function of  $T^{-1}$  from the transcendental equation—

$$\log_{10} \left( \frac{a_1}{N_1} \right) = \frac{k (1 - N_1)^2}{T}$$

is very laborious, though in no sense difficult; it may be carried out either graphically or by successive approximation. Substitution of experimental data for the steam point yields a value of 465 for  $k$ . The curve for this value reproduces the observed values of the solubility of silver in mercury very closely up to the boiling point of mercury, and even above this where it diverges from

<sup>5</sup> Schröder, *Z. Phys. Chem.*, **11**, p. 449, 1893.

<sup>6</sup> Jones, *Proc. Roy. Soc. (A)*, **141**, p. 225, 1934.

<sup>7</sup> Scatchard, *Chem. Reviews*, **3**, p. 329, 1931.

<sup>8</sup> Heitler, *Ann. Physik*, **88**, p. 630, 1926.

<sup>9</sup> Van Laar, *Z. Phys. Chem. (A)*, **137**, p. 421, 1928.

<sup>10</sup> Guggenheim, *Proc. Roy. Soc. (A)*, **148**, p. 304, 1935.

<sup>11</sup> Rushbrooke, *Proc. Roy. Soc. (A)*, **166**, p. 296, 1938.

<sup>12</sup> Hildebrand, "Solubility," New York, 1936, 2nd Edition, Chap. IX and X.

<sup>13</sup> Butler and Harrower, *Trans. Faraday Soc.*, **33**, p. 171, 1937.

the experimental plot it retains an analogous reversed-S form as given by Hildebrand's theory.<sup>12</sup> In view of the fact that two peritectic compounds are formed in this interval of correspondence and that the solid solubility of silver in the mercury lattice is as high as 50% (Day and Mathewson),<sup>14</sup> this excellent agreement with theory is regarded as very encouraging. In Fig. 3 are included the established data for the solubility of silver in liquid tin, which give a roughly parallel plot. Mortimer<sup>17</sup> has also cited a system—toluene-acetanilide—in which, despite the small temperature range available in organic systems, the theoretical reversed-S is exhibited.

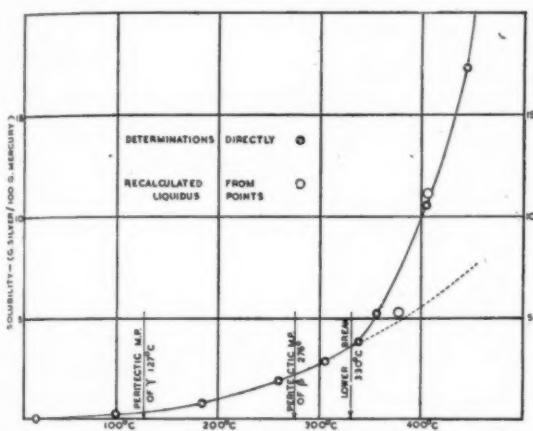


Fig. 2.—Solubility of silver in mercury—direct determinations.

The application of thermodynamical equations to metallic systems has not hitherto found much favour amongst investigators, and it is not difficult to trace the reason for this in the large number and variety of intermediate phases, stable sometimes over small ranges of temperature, which seem to obey no known valency relations and are, indeed, probably not governed by ordinary rules of combination. The existence of solid solubility (substituent and interstitial) and the recalcitrance of many pairs to reach equilibrium, are two other difficulties.

A relatively simple correction can, however, be applied for solid solubility: the expression  $N$  in all the equations considered is replaced by  $N_L/N_S$ . For calculation this is not at all convenient, and it is much easier to plot experimental values not as  $\log_{10}N$ , but as  $(\log_{10}N_L - \log_{10}N_S)$ , in this way thermodynamic requirements are fully satisfied. In Fig. 3, therefore, the theoretical curve should be compared with the experimental curve corrected for solid solubility. The corrected value of  $k$ , again calculated from the experimental data at the steam point, is found to be 388, and the curve for the theoretical equation has also been drawn. Agreement between computed and observed solubility is even better than in the case of the uncorrected solubility, as one would reasonably expect.

Using his rather complicated and at first sight discouraging equation, Hildebrand<sup>12</sup> has achieved notable success in forecasting the solubilities of iodine, stannic iodide, and phosphorus in organic and inorganic solvents.

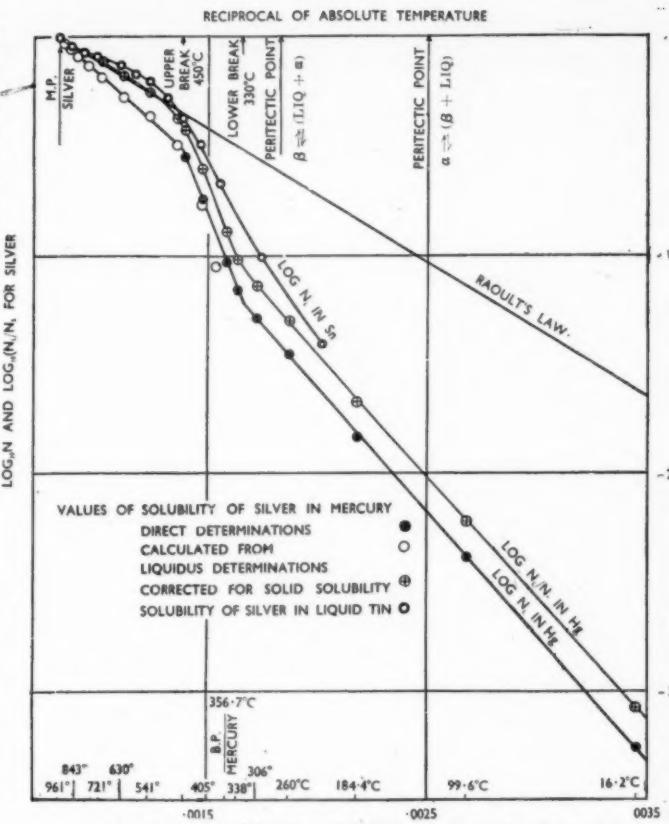


Fig. 3.—Logarithmic solubility of silver in tin and in mercury.

Progressive degradation from the ideal solubility, as the difference between internal pressure of solvent and solute increases, is well illustrated in Fig. 1, plotted from his data. Several methods are available for computing or estimating internal pressure—e.g., surface tension or surface energy, heat of vaporisation, the ratio of the coefficients of expansion and compressibility, the coefficient of expansion, the van der Waals "reduced" equation of state, the van der Waals "reduced" equation (Richards' intrinsic pressure).<sup>16</sup> Unfortunately, the position is still far from happy. Some of these are approximate at best, others can give only relative and no absolute values, many involve small physical coefficients known to no great accuracy owing to difficulty of measurement. Nevertheless, a difference term, in which the method is to some extent eliminated, should show more concordant results. Owing to lack of data, the calculation depending on the van der Waals  $\alpha$  cannot be used. The other methods, in order, give values of 23.8, 40.9, 15.5 (?), 18.2, —, 39.1. The scatter is uncomfortably wide. On the other hand, if  $k = 465$  (for the uncorrected plot) the data give a value of 14 from solubility; if  $k = 388$  (from the observed data corrected for solid solubility—i.e.,  $N_L/N_S$  instead of  $N_L$ ) the value is 12.8. Thus the deviation from ideal

14 Day and Mathewson, *Amer. Inst. Min. Met. Eng. Tech. Pubn.*, **884**, 1938.

15 London, *Z. Physik*, **63**, p. 245, 1930; *Z. Phys. Chem. (3)*, **11**, p. 222, 1930.

16 Richards, *J. Amer. Chem. Soc.*, **48**, p. 3063, 1926.

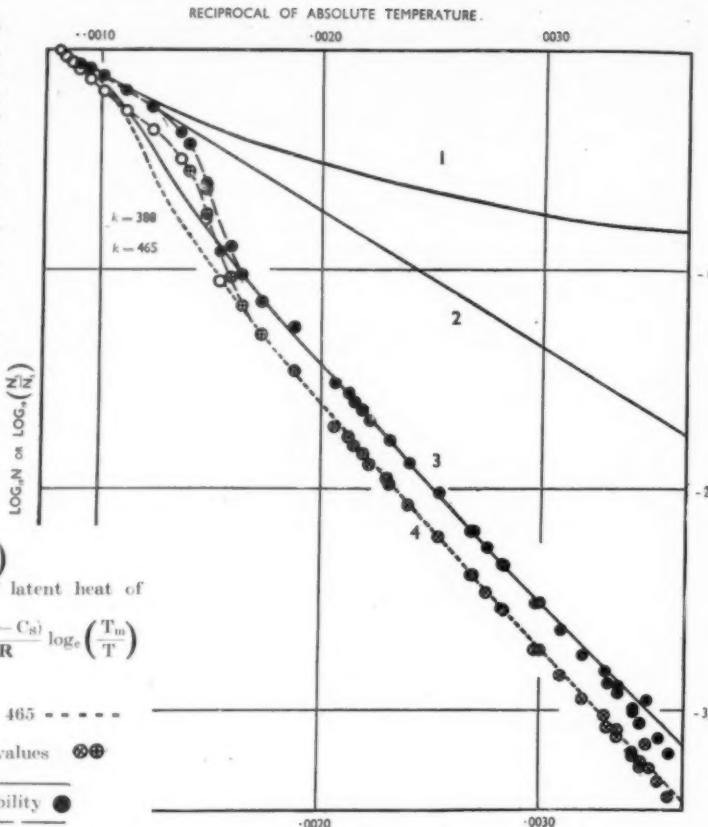
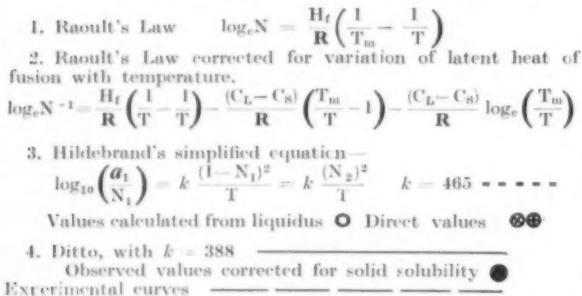
17 Mortimer, *J. Amer. Chem. Soc.*, **45**, p. 633, 1923.

18 Murphy, *J. Inst. Met.*, **46**, p. 507, 1931.

19 Fowler and Rushbrooke, *Trans. Faraday Soc.*, **33**, p. 1272, 1937.

behaviour is only a half or third of that computed from pure physical properties. This is a great improvement on the behaviour of most organic pairs which generally show deviations much greater than those given by theory; in accordance with the prediction of London<sup>15</sup> on theoretical grounds. Even so, the solubility of silver in mercury at room temperature is less than a fortieth of that which would obtain if the solution obeyed Raoult's law. This is consistent with the existence of  $\beta$  ( $\text{Ag}_5\text{Hg}_4$ ) and  $\gamma$  ( $\text{Ag}_5\text{Hg}_8$ ) in well-formed lattices. Even above the peritectic melting points, cybotaxis will presumably still be able to maintain a preponderance of B atoms in the immediate neighbourhood of an A atom.

Fig. 4.—Comparison of experimental values with theoretical curves for solubility.



## Forthcoming Meetings

### The Institute of Metals

The thirty-fifth annual autumn meeting will be held on Wednesday, September 22, at 4, Grosvenor Gardens, London, S.W. 1, beginning at 3 p.m. Following the opening formal business, the following papers will be presented for discussion:—

- “New Methods for the Examination of Corroded Metal.” By F. A. Champion.
- “The Surface Protection of Magnesium Alloys.” By N. Parkinson and J. W. Cuthbertson.
- “The Structure of Rolled and Annealed Aluminium as Revealed by X-rays.” By E. E. Spillet.
- “Directional Characteristics of Single-Texture-Structure Copper Strip.” By Maurice Cook and T. Ll. Richards.

### The Iron and Steel Institute Joint Meeting in Manchester

ARRANGEMENTS have been made for a joint meeting of the Manchester Metallurgical Society, the Institute of Metals and this Institute, to be held on September 29, 1943, at 6.30 p.m., at the Engineer's Club, Albert Square, Manchester, at which Dr. W. H. Taylor will give a lecture on “Lattice Structures in Relation to Physical Properties of Metals.”

It is expected that the President of the Manchester Metallurgical Society will be in the chair.

### Electro-Depositors' Technical Society

THE opening meeting of the above Society will be held at the Northampton Polytechnic, St. John Street, Clerkenwell, London, E.C. 1, on September 27th, at 6 p.m., when the President, Dr. J. R. I. Hepburn, will deliver his address on the subject of “Alloy Deposition.”

### North-East Coast Institution of Engineers and Shipbuilders Diamond Jubilee Session

THE first meeting of the 60th Session of the above Institution will be held on October 15, at Bolbec Hall, Newcastle-on-Tyne, when Mr. J. Ramsay Gebbie will begin his second year of office as President and will deliver an address. The fact that this Institution will be entering its “Diamond Jubilee Session” will add greatly to the interest of this meeting, especially since the maritime strength of the nation is due, in a large measure, to the contribution of the North East Coast, in which this Institution has played an important part.

### Sheffield Metallurgical Association

A JOINT meeting of the above Association and Sheffield Society of Engineers and Metallurgists will be held at the Royal Victoria Station Hotel, on September 28 at 6 p.m., at which Sir Lawrence Bragg, O.B.E., F.R.S., will speak on “The Strength of Metals.” Dr. W. H. Hatfield, F.R.S., will occupy the chair and will be supported by Mr. G. Glenn.

# Non-Ferrous Metals and Alloys for War Purposes

## War Emergency Specifications to Conserve Supplies

*Restrictions in supplies of non-ferrous metals have necessitated stringent economies in their use. In order to conserve and make the best use of those available, new emergency specifications have been issued, and some degree of rationalisation has been effected. These are reviewed, so that fairly complete information regarding them may be available for convenient reference.*

THE enormously increased demand for non-ferrous metals during the last four years for war purposes, together with the restriction of supplies of virgin metals available have made it necessary for the most stringent economies to be effected in their use. The need for conservation and economy applies to all non-ferrous metals and alloys to a greater or less degree, and it has been met to a certain extent by the preparation of new war emergency specifications and by a certain degree of rationalisation. The work of preparing new specifications has been carried out by the Non-Ferrous Metallurgy Industry Committee of the British Standards Institution, by the Non-Ferrous Metals Control, and by certain Service departments.

Rationalisation so far as copper alloys are concerned has resulted in the production of a Services Schedule of non-ferrous metals and alloys for armaments and general engineering purposes, drawn by a conference of the technical representatives of various Government Departments, together with those of several manufacturing firms, convened by the Superintendent, Technical Applications of Metals, Ministry of Supply. Much assistance has also been given by the British Standards Institution, the British Non-Ferrous Metals Research Association, and the Copper Development Association. Economy of tin in plain bearings and bearing metals has been the subject of a report drawn up by a Technical Advisory Committee appointed by the Ministry of Supply and the Tin Research Institute.

### War Emergency Specifications

New emergency specifications have been prepared by the British Standards Institution during the last two years for copper alloys, silicon bronze, high-tensile bronze, and phosphor bronze ingots and castings, as well as for high-tensile brass bars, sections and forgings. The main object of these specifications has been to economise in the consumption of tin in copper alloys either by producing alloys of a lower tin content than those commonly in use or by using alloys free from tin. This need has been caused by the scarcity of tin, as approximately one-third of all the tin used in this country goes into copper alloys. The necessity also of using the supplies of brass and bronze scrap which are available from machining operations and other sources has also been taken into account in preparing the various specifications.

To assist users to meet the urgent need for tin conservation, a new range of standards for copper alloys,

ingots and castings Nos. 1021-1028 were prepared and issued by the British Standards Institution in 1942 at the request of the Non-Ferrous Metals Control. Specifications for alloys free from tin which may be used with advantage for special purposes if produced by manufacturers having experience of such alloys are silicon bronze B.S. 1029-30 and aluminium bronze B.S. 1031-32 and 1072-1073. These new war emergency specifications for bronzes, brasses and tin-free copper alloys are summarised in Table I.

For the duration of the war, it is proposed that Admiralty gunmetal, 88/10/2, B.S. 382/383, should be severely restricted, and that gunmetal 87/9/3/1, B.S. 900/901 should not be used. The 88/8/4 alloy is recommended as a suitable substitute for 88/10/2 gunmetal, but is to be used only for very special applications and for its manufacture virgin metal must not be used. For castings suitable for general purposes subject to medium steam pressures (above 100 lb. per sq. in. working pressure) and at temperatures not exceeding 500° F. (260° C.) and for certain highly loaded unlined bearings and for high-grade backings of lined bearings, the 86/7/5/2 alloy is recommended, while for general purpose castings subject to steam pressures up to 100 lb. per sq. in. working pressure and temperatures not exceeding 400° F. (205° C.) and water pressures up to 200 lb. per sq. in. working pressure and for well-supported backings of certain lined bearings the 85/5/5/5 alloy, B.S. 897/898, is considered suitable. Where tin-base alloys can be dispensed with, Type A and B brass are to be used.

Both the aluminium bronze alloys, B.S. 1031/32 and 1072/73, are suitable for high-strength, high-temperature castings, and are available for replacing tin-bearing alloys for many purposes, particularly as they are very resistant to sea-water corrosion. The war emergency specification B.S. 1029/30 for silicon bronze covers such specific alloys as P.M.G. and Everdur. B.S. 207/208 for special brass ingots and castings also gives an alloy suitable for many purposes, and is substantially free from tin. In 1942, two new war emergency specifications, Nos. 1058/1061, for phosphor bronze and leaded bronze ingots and castings were issued by the British Standards Institution. The first alloy which is specified for all high-duty work, especially for aircraft purposes, contains not less than 10% of tin and 0.50% of phosphorus, while the second alloy, which contains 6.5 to 8.5% of tin, 2 to 5% of lead, not more than 2% of zinc, and not less than 0.3% of phosphorus, and which should be

TABLE I.—WAR EMERGENCY BRITISH STANDARD SPECIFICATIONS FOR COPPER ALLOYS.

Type.	No.	Composition.										Mechanical Properties.	
		Cu.	Sn.	Zn.	Al.	Fe.	Mn.	Ni	Pb.	Si.	Other Elements.		
Gunmetal 88-8-4	1021	Remain	7.5	3.5	—	—	—	1.0 max.	0.5 max.	—	0.15 max.	16.0	8-12
	1022		8.5	4.5									
Gunmetal 86-7-3-2	1023	Remain	6.0	4.0	—	—	—	1.0 max.	1.0	—	0.5 max.	14.0	8-12
	1024		8.0	6.0					3.0				
Brass Type A	1025	70.0	2.0	—	—	—	—	1.0 max.	1.0	—	Fe 0.75 max. Al 0.01 "	11.0	15-20
	1026	80.0	max.	—	—	—	—		4.0				
Brass Type B	1027	62.0	2.0	—	—	—	—	1.0 max.	1.0	—	Fe 0.75 max. Al 0.25 "	11.0	10-12
	1028	70.0	max.	—	—	—	—		4.0		Al 0.25 "		
Silicon Bronze	1029	Remain	—	5.0 max.	—	2.5 max.	1.5 max.	—	—	1.5 3.0	0.5 max.	20.0	15-0
	1030												
Aluminium Bronze	1031	Remain	—	0.5 max.	8.5	1.5	1.0 max.	1.0 max.	—	—	0.3 max.	32.0	20-0
	1032				10.5	3.5							
High Tensile Aluminium Bronze	1072	Remain	—	0.5 max.	8.5	3.0	3.0	3.0	—	—	0.3 max.	40.0	12-0
	1073				10.5	5.5	max.	5.5					

made as far as possible from scrap, is recommended as a substitute for higher grade phosphor bronzes for many purposes.

With regard to wrought non-ferrous alloys, a new war emergency specification B.S. 1000/1002, has been issued for high-tensile brass bars and sections suitable for forging, and also for two types of high-tensile brass forgings, one suitable for soldering and the other not suitable for soldering. From the results of the experience gained by the use of these specifications during the war period it is hoped a definite standard will be established for them at a later date. A number of D.T.D. specifications have also been issued for silicon brass and chromium-nickel-silicon brass in the form of rolled sheet, strip, foil and tubes; for phosphor bronze and chromium bronze in the form of sheet and strip, tubes, rods and wires; for aluminium bronze in the form of rods and other forged products, and also for castings; for high-nickel copper alloys in the form of sheet, bars, strip, rods, tubes and wire; and for copper-nickel-zinc alloys (nickel-silvers) in the form of sheet, strip, rods, rivets, tubes and wires. D.T.D. specifications have also been issued for chromium and aluminium alloys and for magnesium alloys, both in their cast and various wrought conditions.

### Bearing Metals

A very important quantity of tin is absorbed in white metal alloys for bearing purposes, and in order to conserve available supplies it has been found necessary to make certain recommendations with regard to the alloys used for particular purposes. A report on the economy of tin in plain bearings and bearing metals has been drawn up by a Technical Advisory Committee of the Ministry of Supply, and the Tin Research Institute and has been widely circulated to all those interested in the production and use of such alloys. In this report, with a view to ensuring that only the adequate proportion of tin is used for each different type of service, white metal bearing alloys have been divided into four groups, according to their tin content, and an exhaustive list of types of bearings has been provided and the appropriate alloy group indicated for each type of bearing.

The four groups into which the tin and lead-base white metals have been divided are (1) 80-92% tin, (2) 68-75% tin, (3) 7-12% tin, and (4) 0-5% tin. Alloys

of group (1) are recommended for use in aero-engines and for main crankshaft bearings and connecting rod big-end bearings in high-speed internal combustion engines and in compression ignition engines for marine main propulsion, and alloys of group (2) for similar bearings and crosshead bearings in stationary compression ignition engines under 700 r.p.m. For camshaft and all other types of bearings in internal combustion engines; for most bearings in steam turbine and steam reciprocation engines, except turbine, rotor and main bearings; and for road vehicle and machine tool transmission shafting and roller and chain conveyer bearings alloys of group (3) are considered suitable. For power transmission shafting and roller used.

To economise in tin, it has also been recommended that in bearings lined with white metal in which no bearing properties are demanded of the backing, steel, brass or tin-free backing materials should be used. Lined bearings in which bearing properties are demanded of the backing, so that such bearings may continue in service after failure of lubrication or after severe wear, may still be made from tin bronzes provided Admiralty gunmetal and higher grade phosphor bronze are not used.

### Services Schedule, B.S./S.T.A. 7

A schedule of non-ferrous metals and alloys has been prepared recently as a statement of the joint requirements of the Services for non-ferrous metals and alloys for armaments and general engineering purposes. This schedule, as previously stated, has been drawn up by a conference of the technical representatives of the various Government Departments, together with those of several manufacturing firms, convened by the Superintendent, Technical Applications of Metals, Ministry of Supply.

Although the tonnage of non-ferrous alloys used is small, when compared with steel, a very large number of alloys are used and are made to numerous Service, British Standard, and private specifications. The rationalisation of the whole field of the non-ferrous metals and alloys requires, therefore, a survey of very considerable magnitude, and in view of the time likely to be involved, it was decided to deal first with the most important group—namely, the copper alloys, Table II—and to publish that group as a basis for the addition of others. Schedule S.T.A. 7, therefore, represents that stage

TABLE II.

COPPER AND ITS ALLOY, GROUP I, SERVICES SCHEDULE B.S./S.T.A. 7.

Series.	Alloy.
C.	Copper (C for Copper).
C.A.	Aluminium bronze (A for aluminium).
C.G.	Gunmetal (G for gunmetal).
C.M.	Manganese bronzes or high-tensile brasses (M for manganese).
C.P.	Phosphor bronze (P for phosphorus).
C.S.	Silicon brasses and bronzes (S for Silicon).
C.Z.	Brasses (Z for zinc).
C.X.	Extra or special purpose alloys (X for extra).

of the work and has been prepared in loose-leaf form to facilitate the addition of subsequent sections dealing with other groups.

The preparation of this schedule has involved consideration of existing British Standard Specifications, and the composition limits of these have been used as far as possible. In general, the alloys in the schedule are defined by composition and mechanical properties, but in a few cases definition is by composition alone. In certain alloys, as in the case of cartridge brass, other requirements, such as grain size, are specified.

Considerable simplification has been effected by reducing the number of specifications to the minimum necessary to cover all essential requirements. Parallel with this reduction in number, simplification in terms has been carried out wherever possible. Particular attention has also been paid to the ruling war-time conditions, which necessitate the economical use of all scrap, and in some cases (where consideration has to be given to the shortage of any particular metal), influence the choice of an alloy for a given purpose. The scrap factor has in some cases involved raising of the maximum value for impurities, where this may be safely done without adversely affecting the properties of the material. In the case of 70/30 cartridge case brass, however, the need for conserving scrap of low lead content, in order to avoid trouble in the hot rolling of this material, has justified a tightening of the restriction on the lead content.

In preparing the schedule, a simple form of nomenclature has been devised which will be adopted throughout the complete schedule. It facilitates reference, avoids the disadvantage of numbers, and facilitates the insertions of new alloys into any part of the classification. The prefix letter C (C for copper) is applied to the whole copper alloy series, which comprise Group I of the Schedule. The second letter indicates to which sub-group of copper alloys an alloy belongs, according to the system given in Table II. A numeral following the two-letter prefix indicates to which particular type of material in that sub-group reference is made. C.Z. 5, for example, indicates cartridge brass in the brasses series. A material so designated may be sub-divided further by the addition of the letters A, B, C, etc., to cover different applications, compositions or mechanical properties. The addition of a suffix -1 has been made in certain cases to cover special requirements involving small differences in composition or mechanical properties.

In the copper C series are included a tough pitch copper and a deoxidised copper, both suitable for hot or cold-working, the latter not being susceptible to cracking when heated in a reducing atmosphere. The Aluminium Bronzes—C.A. Series include four alloys, two wrought and two cast. The wrought alloys are a 95/5 and a 90/10 alloy, the former suitable for hot or cold working, and possessing high ductility, and the latter, in which optimum mechanical properties are obtained by rapid cooling from the hot-working temperature suitable for valve seats, valve guides, etc. The two cast alloys suitable for sand and die-castings are to B.S. Specifications 1032 and 1073. Gunmetals in the C.G. Series include an 88/10/2 alloy for hard-rolled bars, and the four castings alloys 88/10/2, 88/8/4, 86/7/5/2, and 88/5/5/5, whose applications have already been given.

The high-tensile brasses (manganese bronzes) have been standardised for the first time in the C.M. Series of the schedule. This series is given in Table III, and

TABLE III.—ALLOY HIGH-TENSILE BRASSES—C.M. SERIES (MANGANESE BRONZES) SERVICES SCHEDULE B.S./S.T.A. 7.

No.	Description.	Related Specifications.	Composition.							Tensile Tests, Tons per Sq. In.			Elong. %.	Uses.	
			Cu.	Z	Sn.	Pb.	Fe.	Mn.	Al	Other Element	Scribed Proof Stress.	Ultimate Stress.			
CM. 1	Wrought bars and sections.	B.S. 250A	56				0.5	1.0			15 min.	30 min.	20 min.	General engineering purposes suitable for soldering.	
			59	R	0.5	1.0		1.0	2.5	0.5					
CM. 2	Wrought bars and sections.	B.S. 250A	56				0.7	0.5	0.2		15 min.	30 min.	20 min.	Similar to CM. 1, but aluminium hardened non-soldering quality.	
			59	R	0.5	1.0		1.2	1.2	1.2					
CM. 3	Wrought bars and sections.	B.S. 250B	56				0.7	0.5	2.0		18 min.	35 min.	15 min.	General engineering purposes and hot forgings.	
			59	R	0.5	1.0		1.2	2.0	3.0					
CM. 4	A. Wrought bars and sections.	B.S. 250B	57				0.25	1.0	0.5		18 min.	35 min.	15 min.	Suitable for stressed parts exposed to sea-water conditions.	
			61	R	1.0	0.75		1.0	1.25	2.0					
CM. 4	B. Wrought bars and sections.	B.S. 250B	64				0.5	0.2	4.5		18 min.	35 min.	15 min.	Similar, but with higher copper and aluminium content.	
			68	R	—	—		1.0	1.0	5.0					
CM. 5	Castings .....	Metal Class G.	56				0.5	0.5		0.25	1.0	8 min.	20 min.	12 min.	General castings suitable for soldering.
			62	R	0.5	2.0		1.0	1.5						
CM. 6	A. Castings .....	B.S. 208/1	57				0.5		0.5	0.5	1.0	12 min.	28 min.	20 min.	Castings for gun mountings, marine and general engineering applications.
			63	R	0.5	1.0		1.0		2.0					
CM. 7	B. Castings .....	B.S. 208/2	50				1.0	0.5	2.0		1.0	15 min.	30 min.	15 min.	Castings, liable to stress corrosion cracking. CM. 7 is a $\beta$ -structure alloy.
			70	R	0.25	0.25		2.0	2.5	3.0					

\* Tin not to be intentionally added.

shows the various alloy high-tensile brasses standardised, the relevant specifications relating to them and their uses. Previous efforts to lay down identifiable limits of composition for this class of alloys have been made in times of peace, and have been frustrated by the large variety of compositions made commercially for the same mechanical properties. Under war conditions it became imperative by reason of the scrap position and production problems to fix definite alloys, and with the co-operation of industry, the large variety of mechanical test requirements for this class of alloy have been condensed into a rational series.

In the C.P. Series, six phosphor bronzes are included, two for wrought alloys covering annealed and cold-rolled sheet and strip, hard-drawn tubes and wire, and bars, rods and sections; and four for castings of various types, one being for leaded phosphor bronze and a second having a high tin content. All the phosphor bronzes are to British Standard Specification except one, which is to the Admiralty Specification. Equivalent American specifications are given for each alloy. Two silicon brasses and bronzes are included in the C.S. series, the first of these in three varieties, covering bars and rods, sheet and strip, and castings, and the second for hard-drawn tubes.

The brasses, C.Z. Series, consists of fifteen alloys, some sub-divided into two or more varieties, to British Standard, Admiralty and American Specifications. Aluminium brass, 70/30 brass; Admiralty brass, 65/35 brass, 63/37 brass, naval brass, leaded brass, and brass for castings are included. Some of the alloys are used for wrought materials and others for die and other castings. In the classification, the opportunity is taken of bringing together the various requirements often specified separately for the same composition of alloy prepared by different methods. This applies particularly to brass containing 56.5 to 60% copper, C.Z. 9, the most commonly used alloy of the series, and should be of practical value in various connections.

It has also been found necessary to include in the schedule a number of alloys which are not suitable or desirable for general use in present circumstances, or which are normally specified for a special purpose. This class of materials is placed in the C.X. Series, and include along with others such alloys as 80/20 brass, Admiralty high-tensile brass, high-tin bronze, aluminium bronze for die-castings, a silicon-nickel-copper alloy, and phosphor bronze for sand or chill-cast worm-wheels.

A matter closely affecting production of non-ferrous parts is the desirability of utilising the most readily machinable alloy for its purpose. The former practice of relying on a specified set of mechanical properties without regard to other factors, such as composition and effects of subsequent hot or cold working, has obvious disadvantages which have been the source of trouble in manufacture. It has therefore been found desirable, for example, to differentiate between a hard-drawn straight lead brass (C.Z. Series) and an intrinsically hard alloy brass (C.M. Series), which are not necessarily interchangeable, although having similar tensile properties. It is hoped that by the use of the S.T.A. 7 Schedule and the elimination of the alternatives, the same part will be reproducible with general uniformity in properties and with uniform ease of manufacture.

Conditions of supply are laid down, governing all the materials in the schedule and covering inspection procedure, and British Standard tolerances are included through the courtesy of the British Standards Institution. Conditions of supply cover composition; manufacture and tolerances and provision of test-pieces and conditions governing testing for (1) sand chill and die-castings; (2) bars, rods and sections; (3) plate, sheet, strip and foil; (4) tubes; and (5) forgings and stampings; heat treatment; and tests. As regards the mechanical tests, the proof test given in the schedule refers to the load at which the permanent extension must not be greater than 0.2%. This figure has the advantage that it can be determined by the common scribed line method of test, whereas the 0.1% proof stress required by B.S. specification has to be determined by the extensometer. In cases where Brindell hardness values are specified to govern the condition of the material, Diamond Pyramid or Rockwell hardness numbers may be used by agreement. As increased use is now being made of photo-micrographic standards of comparison for grain size, and in order to facilitate their use, such standards have been included in the schedule by the courtesy of the American Society for Testing Materials.

#### British and American Specifications

In 1942 a summary of British and American Standard Specifications for non-ferrous metals was prepared at the request of the Central Priority Department of the Ministry of Supply and issued by the British Standards Institution as B.S. 1007. In this summary it was originally intended to have established "Tables of Equivalency"—that is, to give a definite indication of what American specifications could be regarded as providing material corresponding to that covered by the relevant British Standard. Owing to the fact that the basis on which the specifications have been framed is not identical in the two countries, in many of the cases it was found impossible to prepare such tables of equivalents. As an alternative, therefore, tables showing the comparative requirements have been drawn up in the hope that they will provide a means whereby each Department or user can assess for themselves the extent to which they can work to American Specification.

These tables, some 35 in all, include aluminium, and its alloys, cadmium alloys; copper and its alloys, lead and lead-base alloys, magnesium and magnesium alloys, nickel, and high and low alloys, nickel alloys, tin and tin-base alloys, and zinc and zinc alloys. All these metals and alloys in their cast and various wrought conditions are dealt with. In the tables, for each metal or alloy are given its composition limits, its British Standard Specification or other British Specification, if any, the American Society for Testing Materials specification, or other American specification, if any, the scope of the specification, and the approximate ultimate tensile strength in lbs. and in tons per sq. in.

The specifications included in the tables are the British Standards Specifications, general series and aircraft series; the Ministry of Aircraft Production material specifications, D.T.D. series; the American Society for Testing Materials (A.S.T.M.) specifications, the U.S. Federal Government specifications, the Society of Automotive Engineers (S.A.E.) specifications, and the Aeronautical Material Specifications (A.M.S.).

# Heat Utilisation in the Steelworks

By R. J. Barritt, M.A.

*Much valuable work on the economical use of fuel has been done by the British iron and steel industry. It is appreciated that the full and complete utilisation of the gases and waste heat on a plant produces a very real and substantial contribution toward reduction of working costs, and enables control to be applied to every department of the works. In this article attention is directed to heat utilisation in a composite plant, especially as it applies to the steelworks part.*

THE steelmaking process reduced to its essentials comprises the reduction of the iron ore by coke in the blast furnace, followed by treatment of the resulting iron (plus scrap) in the steel furnaces to give a steel of the desired composition. The steel so formed is poured into ingot moulds and the ingots in due course are shaped mechanically in the rolling mills to the desired product or intermediate product. In the processes up to the manufacture of pig iron in the blast furnace a surplus amount of heat is available since both the coke ovens and blast furnaces produce more gas than they themselves use in their own processes. The stages following the pig-iron manufacture all require heat to be supplied from external sources, in addition to which heat has to be supplied for steam raising for essential services and for power production. The external sources of heat may be coal, producer gas or the surplus gases from the coke ovens and blast furnaces. Without attempting as yet any balancing of the various heat requirements of the different sections of the process, it is evident there are good grounds for locating the blast furnaces and coke ovens at the same place as the steelmaking equipment from a heat economy point of view, and, provided the advantages in this respect outweigh any transport difficulties which may arise, the composite coke, iron and steel plant would seem to hold advantages over any other combination.

Iron ore, coking coal and limestone do not normally occur sufficiently close to each other to avoid transport of one or the other wherever the works may be situated. For a composite works as described above, the works may be situated near the ore mines with the coal being transported (e.g., Lincolnshire), near the coal mines with the ore being transported (South Wales), or at some intermediate point between ore and coal mines with both being transported.

## Separate Units

Where the units are separated the coke ovens can be situated at the collieries and the coke transported to the blast furnaces, which are situated either near the ore mines or near the coast, so that imported ore can easily be brought in. This last arrangement was not uncommon in this country, but the reorganisation of the iron and steel industry which took place in the eight years or so immediately before the war favoured the composite iron and steel works with the coke ovens situated at the steelworks and not at the collieries. The justification for this lies almost entirely in the heat economies which can be obtained by the grouping of all the units at one site. With the modern steelworks it is quite likely that the only raw coal used in the works is that from which

coke is made at the coke ovens and all the heating in the works is done by coke-oven or blast-furnace gas.

This development entailed a central department whose job comprised accepting fuel from two departments in the steelworks and allocating the appropriate fuel or mixture of fuels to all departments, together with responsibility for pipe-lines and distribution, etc. This, in turn, demands a fair knowledge of the various processes and their heat requirements and accounts for the transition of the "B.th.u. chaser" of the old days into the rather more resounding "Fuel and Economy" department or similar title. The second half of the title is no empty name, since an excessive use of fuel in any one department is liable to put the whole works out of balance. The Fuel Department's activities concern the whole works, and the head of that department, in addition to possessing a good general knowledge of all the steelworks processes and being technically competent, must possess a fairly high degree of tact.

## Composite Works

In a composite iron and steel works, then, the fuel supplies available are coal, coke-oven gas (about 500 B.th.u.'s per cub. ft.), blast-furnace gas (about 100 B.th.u.'s per cub. ft.), and generally it is desirable that the use of raw coal as a fuel should be reduced to a minimum whether used as coal direct or after conversion to hot tarry producer gas.

The units to be supplied with heat in a typical case would be the coke ovens, blast furnaces, steel furnaces, soaking pits and reheating furnaces, together with the boilers for providing process steam and generating power. Of these the coke ovens and blast furnaces normally both provide and use gas at a fairly constant rate. The gases produced, however, are, of necessity by-products of the main ironmaking process, and the quantities cannot be varied to suit changes in demand from other parts of the works without the "make" of iron or coke being affected. The demands of some of the users fluctuate considerably, and the first necessity for efficient fuel utilisation in the steelworks is adequate gas-holder capacity for both coke-oven and blast-furnace gas to prevent wastage of gas.

Some of the fluctuations are too large to be met by gas-holders of economic size, and to meet these larger fluctuations one or more of the fuel-consuming units has to be capable of changing over its means of heating from one form to another fairly rapidly or of varying the ratio of different fuels used for heating. In normal cases this might conveniently be the boilers which are amongst the largest fuel consumers and which could be

arranged for heating by coke-oven or blast-furnace gas or solid fuels. The coke ovens are also capable of being heated by coke-oven or blast-furnace gas without an excessive amount of trouble in valve-changing, and are also used quite extensively as a buffer to control the amounts of the two gases available.

Opinions on adequate holder size vary considerably (although nobody on the operating side has ever been heard to say that there is sufficient holder capacity). Coke-oven gas holders vary from a mere balancing holder upwards, but normally a half-hour storage capacity based on the total gas made would seem to be the minimum desirable and most operating engineers would like double this amount. Wide variations are also found in blast-furnace gas-holder requirements, but with a large works having a number of furnaces the convenient minimum holder capacity would seem to be about equal to one hour's gas-make from the largest furnace. As stated previously, these gas holders only smooth out the smaller fluctuations and larger variations in supply and demand must be met by adjusting the ratio of the various fuels supplied at one or more of the units.

Possible fuels for the different units in the steelworks are as follows:—

(1) Blast furnaces .....	Blast-furnace gas at stoves.
(2) Coke ovens .....	Blast-furnace gas, coke-oven gas. (Producer gas from coke is possible, but unlikely at a steelworks.)
(3) Open-hearth furnaces .....	Coke-oven gas alone, or mixed with blast-furnace gas, or mixed with hot coal producer gas, or producer gas alone.
(4) Soaking pits .....	Coke-oven gas, blast-furnace gas, producer gas, or mixed gas from any two.
(5) Reheating furnaces .....	As for soaking pits.
(6) Boilers .....	Blast-furnace gas, coke-oven gas, coal as pulverised fuel or stoker-fired, and coke breeze.

It will be noticed that coke-oven gas and blast-furnace gas occur in all six items; consequently if these are available in sufficient quantity the steelworks will be self-supporting from a fuel point of view. As an alternative to part of the boiler capacity, gas-engine generators driven by blast-furnace gas could be used for power supply to the works. Some very large gas-engine units have been installed in the past, and the efficiency of the gas-engine set is higher than that of the boiler and turbine combination. Gas-engine sets, however, have lost popularity in the newer works in favour of normal turbine sets, presumably on grounds of availability and their inability to use alternative fuels.

#### Allocating Consumption

Having listed the various possible fuels, the next step is to make up a priority list of the different consumers. No alternative fuel exists for heating the checker work in the blast furnace stoves, and the stoves therefore have the first call on the blast furnace gas. If gas-engine blowers were used they would have an even higher priority, and gas-engine generators without an easily available alternative supplier would obviously have a high priority. In the newer works the gas engine problem does not exist as a rule, and the hot blast stoves come first.

The quantity of blast furnace gas available depends upon the coke consumption per ton of iron in the blast furnace, and therefore upon the quality of iron ore being used. About 150,000 cub. ft. of blast-furnace gas is produced per ton of coke used in the furnace. For a rich ore the coke used will run about 18 cwt. per ton of iron made, and the blast-furnace gas will have a calorific value of 95 to 100 B.th.u.'s per cub. ft. The consumption of blast-furnace gas in the hot-blast stoves will be

about 22% of the gas made in the furnace. With a lean ore—e.g., Lincolnshire—the coke consumption per ton of iron is about 27 cwt., the calorific value of the gas produced is somewhat over 100 B.th.u.'s per cub. ft., and the consumption of blast-furnace gas in the stoves about 18%. It will be noted that for a particular output of iron the works using lean ores in the blast furnaces will have about 50% more coke-oven and blast-furnace gas available than those using rich ores.

The coke ovens produce about 11,000 cub. ft. of gas of calorific value about 500 to 540 B.th.u.'s per cub. ft. (gross). To carbonise 1 lb. of coal in the coke oven requires about 1,050 B.th.u.'s gross, and this can be provided by coke-oven gas, in which case some 2 cub. ft. will be required per lb. of coal, or by blast-furnace gas, in which case 10½ cub. ft. will be required. A battery of coke ovens carbonising, say, 1,000 tons of coal per day, would comprise about 50 ovens each being a horizontal chamber about 40 ft. long, 14 ft. high, and 16 in. to 18 in. wide. These chambers hold about a 16-ton charge of coal and the carbonising is completed in about 18 hours. The heating flues form the dividing walls between the various oven chambers and below each oven are located regenerators divided normally into two or three parts.

When using coke-oven gas for heating the ovens, the air for combustion is preheated in the upstream regenerators before meeting the coke-oven gas at the base of the heating flue. Combustion takes place upwards in the heating flue, which corresponds approximately to the full height of the coal charge and the products of combustion pass down a neighbouring flue and into the downstream regenerator and into the chimney flue. Approximately every half hour the direction of heating is reversed and the upstream and downstream regenerators are changed over automatically.

When blast-furnace gas is used for heating the ovens, both the gas and combustion air are preheated—i.e., if the upstream regenerator is divided into two parts, one part will preheat the blast-furnace gas and one the combustion air, while the corresponding two parts of the downstream regenerator will both abstract heat from the products of combustion. Possible leakage of blast-furnace gas from the upstream regenerator into a downstream regenerator is obviously to be avoided, and the coke-oven designers usually try to arrange the regenerators so that the upstream air regenerators are interposed between the blast-furnace gas regenerator and the downstream waste gas regenerator.

Since each oven has its own regenerator, any number of ovens in the battery can be heated with coke-oven gas or blast-furnace gas as desired. The change over from coke-oven to blast-furnace gas heating involves an alteration to the waste gas reversing valves, so that blast-furnace gas is introduced to the appropriate part of the regenerator instead of air, the shutting off of the coke-oven gas and the linking up of the blast-furnace gas valve to the reversing mechanism. If the ovens are changed individually a battery of 50 ovens would take about 25 mins. to change over completely from one form of heating to the other.

The coke ovens therefore are quite commonly used to balance the coke-oven and blast-furnace gas requirements—i.e., if too much blast-furnace gas is available and too little coke-oven gas, more ovens would be fired with blast-furnace gas to release the corresponding

quantity of coke-oven gas. As a point of minor interest, the volume of combustion products when firing with blast-furnace gas is higher than is the case with coke-oven gas, and the stack loss is somewhat greater, giving slightly less efficiency than with coke-oven gas heating, particularly if the nett calorific value is used for comparison. If the gross calorific value is used there is very little difference in the two methods of heating.

Coke ovens can also be heated with producer gas from coke producers as indeed is the case at gasworks, but there is little point in using up coke made for the blast furnaces in producers. The blast furnaces normally use all the coke over about 1 in.-1½ in. cube in size, the remainder being screened out and sold for domestic purposes. Yields with different coals vary, but a typical figure is blast-furnace coke 65% on dry coal charged to the ovens and smaller sizes 7%. To heat the ovens with producer gas requires a quantity of coke to the producer about 15% by weight on the coal charged to the oven—i.e., about half the battery could be heated by producer gas from the small sizes of coke if desired. To make this a reasonable proposition, however, the price of domestic coke would have to fall so that the producer gas could be made for less than 1½d. per therm, which is the cost of an equivalent fuel elsewhere in the works (hot gas from coal producers at open-hearth furnaces). The price of small coke has never reached this low level as yet, and coke producers for providing fuel gas for coke ovens are not used in iron and steelworks.

The open-hearth furnaces at the steel plant are the largest users of fuel in the works, apart from the boilers, and usually the largest users of coke-oven gas. A luminous flame is an advantage at the open-hearth furnace, and this can be obtained with coke-oven gas alone with preheated air from the regenerators. Tar burners are frequently used in addition to the main gas burners, to give a still more luminous flame. Where mixed gas is used the gas is also preheated in the regenerators, causing partial decomposition of the hydrocarbons and giving rise to a luminous flame. Addition of coke-oven gas to give a calorific value of about 230 B.th.u.'s per cub. ft. for the mixture is about normal practice. If mixed gas is used the calorific value of the mixture should be automatically controlled. In contrast to the blast furnaces and coke ovens, which work continuously, the open-hearth furnaces, in common with the rest of the steel plant, work about a 5½-day week. Heat consumption figures vary somewhat with circumstances, but in the absence of other data a figure of 5·5 to 6 million B.th.u.'s per ton of ingots will serve as an approximation.

For the soaking pits, blast-furnace gas is normally favoured or a low calorific value mixed gas, and both gas and air are preheated in regenerators. Heat consumptions vary in different cases, but about 1·5 million B.th.u.'s per ton can be assumed for approximate purposes.

For the reheating furnaces and heat-treatment any of the gases available can be used, probably a mixed gas for the reheating and coke-oven gas for heat-treatment. As for the open-hearth furnace, if mixed gas is used the calorific value should be automatically controlled. The heat consumption is about the same as for the soaking pits—i.e., 1·5 million B.th.u.'s per ton throughput, but the throughput will of course be less,

since only a portion of the total steel made is reheated for re-rolling or heat-treated as the case may be.

Before being able to arrive at the total heat requirements for the whole works, it is necessary to know the process steam quantity and power used to be able to assess the fuel requirements at the boilers. The blast furnaces are the chief process steam users, and requirements vary a good deal in different localities, but about 2,000 lb. per ton of coke charged will serve as a very approximate figure. The coke ovens as the next largest user account for about 400 lb. of steam per ton of coal carbonised, or about 620 lb. per ton of blast-furnace coke, giving a total of, say, 2,700 lb. of steam per ton of blast-furnace coke. A further 15% goes to miscellaneous smaller users, and the total is about 3,100 lb. per ton of blast-furnace coke used.

The power used on the blast furnaces varies with the total material throughput—i.e., chiefly with the nature of the ore, but keeping on a coke basis for convenience, about 45 k.w.h. per ton of coke charged can be used, together with a further 15 k.w.h. at the coke ovens. Taking a round figure of 100 k.w.h. per ton of ingots for the steel furnaces and rolling mills, sufficient data is available to arrive at a total power figure for the works, which can be reduced to steam and fuel requirements by using appropriate efficiency factors.

The choice of boiler pressure depends upon whether the process steam is passed out at about 200 lb. per sq. in. or less, let down to this figure, or generated at the appropriate lower pressure, since the quantity of process steam usually exceeds the steam requirements of the generators. The modernised steel plants have mostly favoured higher pressure units capable of being fired with either coke-oven gas, blast-furnace gas or pulverised fuel. Since the boilers are the largest fuel user in the works and can operate on any of the available fuels, they form a very convenient balancing point for the whole works—i.e., adjusting the ratio of gases available elsewhere, and in case of gas shortage burning pulverised fuel in addition to the gas to comply with steam requirements. Sharp changes in fuel requirements elsewhere in the works cannot be taken up instantaneously at the boilers, and one of the main functions of the gasholders is to look after these changes until the necessary adjustments are made.

#### Fuel Requirements

We are now in a position to examine the fuel requirements of the blast furnaces and coke ovens as one section of the works and the steel plant as the other. Then by fixing the ratio of iron used to the total steel ingot made the composite works can be considered. In the figures below the power has been taken as being generated in a condensing turbine set, and it should be remembered that a more efficient arrangement than this is possible, using higher pressure steam for power generation and to drive turbine blowers, etc., with the appropriate amount of process steam being bled off at the desired pressure. Much more detail of steam-using equipment would be needed to work this out than is available for a general case, such as is being considered here.

(1) Blast furnaces and coke ovens per thousand tons of iron per week. (Blast-furnace coke on coal charged to ovens 65% ; 11,000 cub. ft. coke-oven gas per ton of coal ; 150,000 cub. ft. blast-furnace gas per ton of coke.)

	Rich Ore.		Lean Ore.	
Coke consumption per ton of iron, cwt.	18	..	27	..
Coke per week, tons	900	..	1,350	..
Coke per hour, tons	5.35	..	8.02	..
Coal per hour to coke ovens, tons	8.23	..	12.35	..
Coke-oven gas per hour, cub. ft.	90,500	..	135,750	..
Therms per hour in C.O. gas	471	..	706	..
Blast-furnace gas per hour, cub. ft.	803,000	..	1,204,000	..
Calorific value, B.t.u./cub. ft.	95	..	105	..
Therms per hour in B.F. gas	762	..	1,265	..
Total therms from ovens and furnaces	—	1,233	—	1,971
% B.F. gas to stoves	22	..	18	..
Therms per hour to stoves	168	..	228	..
Therms per hour to coke ovens	194	..	291	..
Total therms to ovens and furnaces	—	362	..	519
Surplus therms available per hour	—	871	..	1,452
K.w.h. used/hour at coke ovens	80	..	120	..
K.w.h. used/hour at furnaces	240	..	360	..
Total k.w.h.	320	..	480	..
Equivalent steam/hour lb.	3,200	..	4,800	..
Steam used at C.O. hour lb.	3,300	..	4,950	..
Steam used at furnaces/hour lb.	10,700	..	16,000	..
Total steam	17,200	..	25,750	..
Equivalent therms @ 80% off.	—	365	..	547
Surplus therms available after meeting services requirements	—	506	..	905

(2) Steel plant on basis of 1,000 tons of ingots per week.

open-hearth Furnaces—		428 therms per hour
140 hours/week and 60 therms per ton		
Soaking Pits—		—
130 hours/week and 15 therms per ton		115 " "
Reheating Furnaces, etc.—		—
130 hours/week and 15 therms per ton		50 " "
Total therms for heating in steel plant		593 therms per hour.
K.w.h. per hour	715	
Equivalent steam/hour lb.	7,150	
Process steam, etc., /hour lb.	2,000	
Total steam in steel plant, lb.	9,150	
Equivalent therms/hour	—	194
Total heat requirements, therms/hour	—	787

To obtain the picture of a composite coke, iron and steel works we need to know the amount of iron used per ton of steel ingots made, and whether any pig iron is sold as such. Taking purely hypothetical cases for the two types of ore, we can consider works in which the proportion of iron used for steel manufacture is 70% of the steel ingot production. The basis is again per thousand tons of ingots per week.

	Rich Ore.		Lean Ore.	
Therms/hour from C.O. and B.F.	—	610	..	1,016
Therms/hour required for heating steel furnaces	—	593	..	593
Therms/hour for boilers for whole works	—	255	..	383
Total heat requirements	—	1,442	..	1,170
Deficiency therms/hour	—	432	..	154

It will be seen that on this basis neither works is self-supporting without external fuel coming in, and if no pig-iron sales take place the boilers would probably be partly coal-fired during 5½ days of the week and gas-fired at week-ends.

If pig iron is sold in addition to steel more therms are available from the coke ovens and blast furnaces. For the works using rich ore, if 850 tons of pig iron are sold per 1,000 tons of ingots made the fuel production and requirements of the two halves of the composite works balance, and no outside fuel is needed. For the works using lean ore the balance point occurs when 170 tons of pig iron is sold per 1,000 tons of ingots made. In both cases if the coke ovens are separated from the steel works the balance would be very considerably disturbed, and the justification for locating coke ovens at the steelworks is clear.

The above cases are purely hypothetical, and obviously considerable variations can occur in local practice. The methods used, however, should be applicable to in-

dividual cases, and in practically every case it will be seen that the composite works is more favourably placed than any separate combination of its units. For this reason the composite works was favoured when the iron and steel industry was substantially reorganised in the years before this war, and this process will no doubt continue in the future.

## New British Chemical Standards

BUREAU OF ANALYSED SAMPLES, LTD., of Markington, Harrogate, announces that the following new analytically standardised steel is ready for issue:—

B.C.S. MANGANESE-MOLYBDENUM STEEL No. 214.

	<sup>0.01</sup>	<sup>0.01</sup>	
Mn	1.61—	P	0.024
Mo	0.255	Cu	0.24—
C	0.375	Ni	0.16
Si	0.24—	Cr	0.06
S	0.033		

As usual, this steel has been analysed by a number of chemists representing independent analysts and several works' chemists representing manufacturers of this type of steel.

This composition comes within the chemical specification for steel B.S. En. 16-V 9A and will be found useful to chemists wishing to check the composition of steels made to this specification.

In addition to the above, a replacement of nickel steel "T2" has recently been made—viz., 3% nickel steel No. 222 (Ni 3.39%).

The following new standards are in course of preparation:—

Aluminium alloy No. 216, containing approximately Cu 4%, Mn 0.5%, Zn 0.2%, Mg 0.5%, Ni 0.2%, Ti 0.1%.

Cr-Ni-Mo steel No. 219, containing approximately Cr 0.7%, Ni 3%, Mo 0.6%.

High-speed Tungsten Molybdenum steel No. 220, containing approximately tungsten 6%, Cr 4%, V 1.3%, Mo 4.5%.

Further announcements will be made about these in due course.

Supplies may be obtained through the usual chemical laboratory furnishers or direct from the Bureau.

## ERRATA

Page 177 of August issue.

Second line of title, instead of "Bronze" read "Iron."

Page 171.

*Left-hand column.* Fourth line of second paragraph should read:—"coils. Cut lengths are usually stacked so that the plane of."

For "1" in first line of the fifth paragraph read "l".

*Right-hand column.*—In the second equation for "9.08" read "0.08."

Delete "for  $Fe_2O_3$ " in the fifth line of the first complete paragraph, and in the seventh line read "K<sub>t</sub>" for "kt."

Page 178.

*Left-hand column.*—In the third equation read "e" for "E" and "I<sub>s</sub>" and "I<sub>s</sub><sup>1</sup>" for "I<sub>s</sub>" and "I<sub>s</sub><sup>1</sup>".

*Right-hand column.*—In third line of second complete paragraph read "πR<sub>s</sub><sup>2</sup>H" for "πRH<sub>s</sub><sup>2</sup>".

Page 179.

*Left-hand column.*—In first line of third complete paragraph read "thermocouple" for "thermal couple".

# The Constitution of Alloys of Aluminium with Manganese, Silicon and Iron

## III.—The Ternary System: Aluminium-Silicon-Iron

## IV.—The Quaternary System: Aluminium-Manganese-Silicon-Iron

By H. W. L. Phillips, M.A., and Major P. C. Varley, M.A.

*This work forms part of a comprehensive programme of research on the constitution of aluminium alloys carried out in the Laboratories of the British Aluminium Co., Ltd. Earlier work on the constitution of alloys of aluminium with silicon and iron has been revised. The constitution of the quaternary alloys of aluminium, manganese, silicon and iron has been studied over the range manganese 0-4, silicon 0-4, iron 0-4%. The present work is fully described in a paper\* by the author; there it is outlined and some of the results are given.*

### III.—THE TERNARY SYSTEM: ALUMINIUM-SILICON-IRON

THE constitution of the alloys of aluminium with silicon and iron has previously been in the Laboratories of the British Aluminium Co., Ltd., and formed the subject of a paper<sup>1</sup> in 1927. Since that date some solubility measurements made in collaboration with Mr. N. S. Brommelle, B.A., have shown that the temperature previously reported for the primary crystallisation of  $\text{FeAl}_3$  were on the low side, owing to undercooling. The revised liquidus diagram for the range silicon 0-12, iron 0-6% is shown in Fig. 1. There are five primary phase fields, due to aluminium,  $\text{FeAl}_3$ ,  $\alpha(\text{Fe-Si})$ ,  $\beta(\text{Fe-Si})$ , and silicon. The primary aluminium field ABCDEF is bounded by eutectic valleys associated with the separation of binary complexes of aluminium with  $\text{FeAl}_3$  (BC),  $\alpha(\text{Fe-Si})$  (CD),  $\beta(\text{Fe-Si})$  (DE), and silicon (FE). The last two meet at the ternary eutectic point E. The compositions and temperatures previously reported for the invariant points C, D, and E have been confirmed and are as follows:—

$\text{FeAl}_3$  is primary in the concentration region BCHG; it reacts peritectically with the liquid along CH to give the ternary phase termed  $\alpha(\text{Fe-Si})$ , formerly termed  $\beta$ .  $\text{FeAl}_3$  crystallises in the form of long prisms or needles, whether it is primary or secondary, and retains in the ternary alloys the same characteristic colour and etching properties that it possesses in the binary alloys of aluminium and iron. In the concentration region

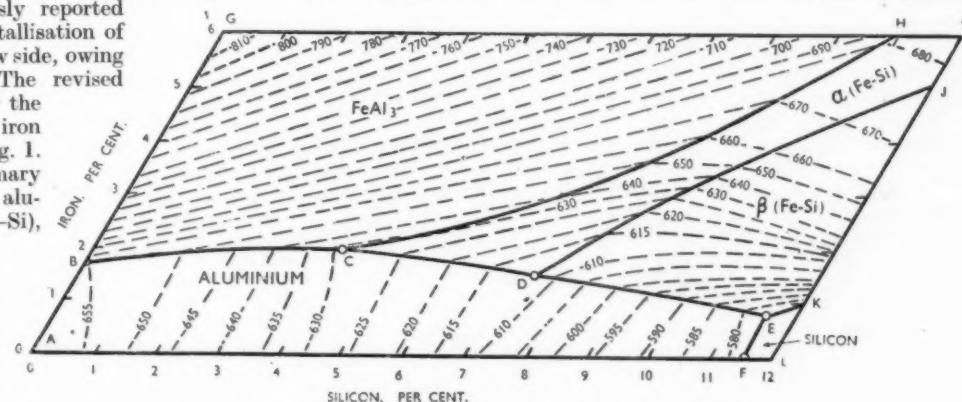


Fig. 1.—Aluminium-silicon-iron alloys: The liquidus.

CDJSH the constituent  $\alpha(\text{Fe-Si})$  is primary. It is paler in colour than  $\text{FeAl}_3$ ; when secondary, it crystallises in the habit frequently termed "Chinese script." It reacts peritectically along DJ to give  $\beta(\text{Fe-Si})$ . The latter constituent is primary in the concentration region DEKJ. It crystallises in the form of needles or plates and is paler in colour than the  $\alpha$  body. Neither of these peritectic reactions proceeds to completion during slow solidification, with the result that envelopment is of frequent occurrence. Crystals of  $\text{FeAl}_3$  are often found wholly or partially surrounded by a sheath of  $\alpha(\text{Fe-Si})$ , and the latter by  $\beta(\text{Fe-Si})$ . On annealing, both  $\text{FeAl}_3$  and  $\alpha(\text{Fe-Si})$  tend to become converted to  $\beta(\text{Fe-Si})$ . The

TABLE I.

Point.	Phases in Equilibrium with Liquid.	Composition.		Temperature °C.
		Iron, % <sup>o</sup> *	Silicon, % <sup>o</sup> *	
C	Al, $\text{FeAl}_3$ , $\alpha(\text{Fe-Si})$ .....	2.0	1.0	629
D	Al, $\alpha(\text{Fe-Si})$ , $\beta(\text{Fe-Si})$ .....	1.5	7.5	611
E	Al, $\beta(\text{Fe-Si})$ , Si (Ternary Eutectic)	0.8	11.6	577

a body is capable of dissolving manganese, and forms a continuous series of solid solutions with the phase  $\alpha$ (Mn-Si) of the aluminium-manganese-silicon system. The  $\beta$  body appears to have little or no solubility for manganese, but, as has been shown previously,<sup>2</sup> it is capable of dissolving copper and forms an unbroken series

of solid solutions with the ternary phase "N" of the aluminium-copper-iron system. Silicon is primary in the concentration region FEKL. The two lines FE and EK are both eutectic lines. Silicon is darker in colour than any of the iron-bearing constituents and rarely presents difficulty in identification.

The surfaces of secondary separation are shown in Fig. 2. In the field in which aluminium and  $\text{FeAl}_3$  are primary, the secondary isothermals are rectilinear and appear to radiate respectively from the aluminium corner and from the point representing the composition of  $\text{FeAl}_3$ . Although it is possible that  $\text{FeAl}_3$  is capable of dissolving silicon, it would seem that the amount dissolved is not large. In the primary  $\alpha$  and  $\beta$ (Fe-Si) fields the secondary isothermals appear to be rectilinear, but they do not radiate from fixed points. It was on these grounds that the conclusion was reached<sup>1</sup> that both bodies are phases of variable composition.

In the concentration region ABC, where aluminium is primary and  $\text{FeAl}_3$  secondary, the peritectic reaction between  $\text{FeAl}_3$  and liquid takes place when the temperature has fallen to  $629^\circ\text{C}$ . and the liquid composition has reached that indicated by the point C. It is only the  $\text{FeAl}_3$  in contact with the liquid that reacts; diffusion is too slow to permit of any appreciable attack of  $\text{FeAl}_3$  already surrounded by solid aluminium. With further cooling, the binary separation is that of the aluminium- $\alpha$ (Fe-Si) complex, and the liquid composition follows the line CD until the point D is reached. Here the second peritectic reaction takes place, at  $611^\circ\text{C}$ ., and, like the former one, it only involves the small amount of reactant—in this case  $\alpha$ (Fe-Si)—actually in contact with the liquid. With further cooling, the liquid composition follows the line DF until E, the ternary eutectic point, is reached, when silicon separates.

Alloys having  $\text{FeAl}_3$  as their primary constituent fall into three groups. In the concentration region BCNG aluminium is secondary and  $\alpha$ (Fe-Si) ternary; the latter separates when the point representing the composition of the liquid, moving along BC, has reached C. From this point onwards the course of solidification is the same as for alloys in the region ABC. In the region CPQN,  $\alpha$ (Fe-Si) is secondary; the primary  $\text{FeAl}_3$  is attacked, but soon becomes enveloped by  $\alpha$ . The point representing the composition of the liquid moves, not along the line PC, but across the field PCD, and reaches the boundary of the aluminium field CD. From this point

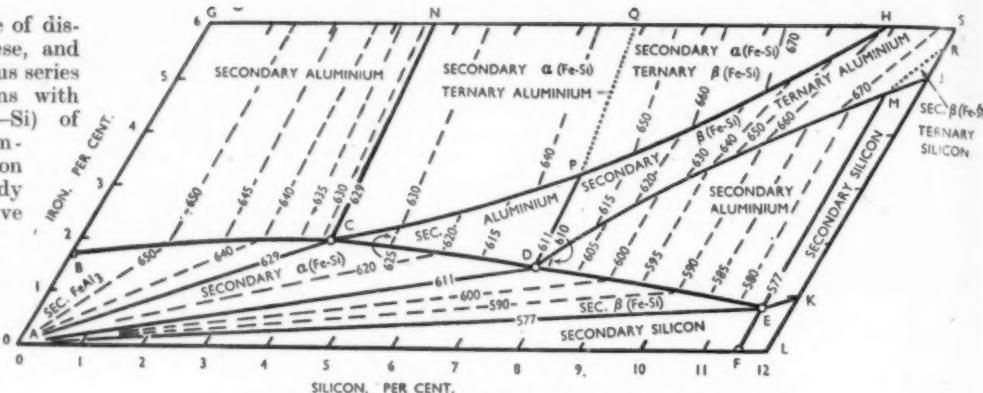


Fig. 2.—Aluminium-silicon-iron alloys. Secondary surface.

onwards the liquid composition follows the line CDE:  $\beta$  is deposited at D and silicon at E. In the region QPH,  $\alpha$ (Fe-Si) is also secondary, but when envelopment of the  $\text{FeAl}_3$  is complete the point representing the composition of the liquid moves across the  $\alpha$  field and reaches the line DJ. Here the second peritectic reaction takes place;  $\alpha$  becomes enveloped by  $\beta$ , and the liquid composition moves across the field DEKJ until the line DE is reached, when aluminium commences to separate.

Alloys of which the primary constituent is  $\alpha$ (Fe-Si) also fall into three groups. To the left of the line PD, aluminium is secondary. In the region DMRSHP,  $\beta$ (Fe-Si) is secondary and aluminium is ternary. To the right of the line MR, the point representing the liquid composition, crossing the field DEKJ, reaches the boundary of the silicon field EK, and hence silicon is ternary. Alloys having  $\beta$ (Fe-Si) as their primary constituent fall into two groups. To the left of the line ME, aluminium is secondary, separating along DE; to the right of this line, silicon is secondary, separating along EK. There is little structural difference between the alloys lying to the left of the line EMR and those lying to the right.

The constitution of the alloys of aluminium with silicon and iron has also been studied by Dix and Heath.<sup>3</sup> Like Gwyer and Phillips, they identified two ternary phases,  $\alpha$ (Fe-Si) and  $\beta$ (Fe-Si), the former crystallising as "Chinese script" and the latter as plates or needles. Fink and Van Horn<sup>4</sup> also described the results of their X-ray examination of the phases of this system. They found that  $\beta$ (Fe-Si) gave a characteristic diffraction pattern, and that its axial ratio varied somewhat according to the composition of the alloy from which the specimen had been extracted. The pattern of  $\alpha$ (Fe-Si) however, was almost identical with that of  $\text{FeAl}_3$ . The lattice parameter of  $\alpha$  was found to be slightly smaller than that of  $\text{FeAl}_3$ , and there were some differences in line intensities. From the work of Bradley and his colleagues it is clear that similarity of diffraction pattern does not necessarily preclude the existence of separate phases. In their work on the ternary alloys of aluminium with iron and nickel, for example, Bradley and Taylor<sup>5</sup> found that  $\text{FeAl}_3(\lambda)$  decomposes on cooling into a mixture of  $\text{Fe}_2\text{Al}_7(\lambda_1)$ , and  $\text{Fe}_2\text{Al}_5(\mu)$ . The main

<sup>3</sup> E. H. Dix, Jr. and A. C. Heath, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, 1928, 164.

<sup>4</sup> W. L. Fink and K. R. Van Horn, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, 1931, 383.

<sup>5</sup> A. J. Bradley and A. Taylor, *J. Inst. Metals*, 1940, 68, 53.

features of the patterns of  $\lambda$  and  $\lambda_1$  are identical, and the differences between them are second-order effects.

The composition of the ternary phases in this system has been the subject of much research during the last 10 years, but cannot yet be regarded as satisfactorily established. Two investigators have reported that only one ternary phase exists, but the majority have found at least two to be present. Some authors have assigned chemical formulae to these phases, whilst others have stated that they are of variable composition. Table II summarises the views that have been expressed. In the opinion of the authors of the present paper, the evidence in favour of two ternary phases is too strong to be disregarded.

TABLE II.

Author.	Ref.	Number and Nature of Ternary Phases Present.
Fuss	6	One: $Al_6Fe_2Si_2$
Nishimura	7	One: $Al_2Fe_5Si_2$
Urasov and Sashin	8	Two: both variable
Sergeev and Rimmer	9	Two: $Al_2FeSi_2$ and $Al_nFe_8$ , where $n = 4$ to 5.
Jänicke	10	Four: $Al_2FeSi_2$ and three others.
Takeda and Mutuzaki	11	Six: those nearest Al corner are $Al_4Fe_2$ and $Al_2FeSi_2$

#### IV.—THE QUATERNARY SYSTEM : ALUMINIUM-MANGANESE-SILICON-IRON

It was decided to study in detail the constitution of alloys lying within the range manganese 0-4, silicon 0-4, iron 0-4%. The difficulty of distinguishing between FeAl<sub>3</sub> and the manganese-rich phases was very considerable, and precluded an extension of the investigation towards higher percentages of iron and manganese. A few alloys were also investigated, the compositions of

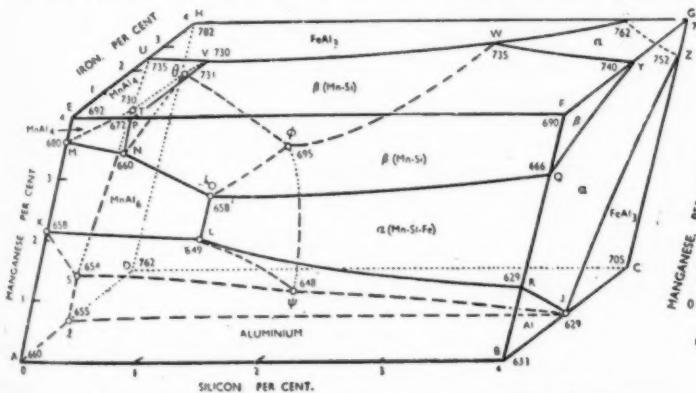


Fig. 3.—Aluminium corner of the quaternary system : The liquidus.

which lay near to the ternary eutectics aluminium-silicon- $\alpha$ (Mn-Si) and aluminium-silicon- $\beta$ (Fe-Si).

No new quaternary constituent was met with, and all the phases could be traced back to the binary or ternary systems. There is no quaternary eutectic in these alloys ; solidification is completed at one or other of the two ternary eutectics. The constituents present are given as follows : Aluminium,  $MnAl_3$ ,  $MnAl_5$ ,  $FeAl_3$ , silicon,  $\alpha(Mn-Si)$  and  $\alpha(Fe-Si)$ ,  $\beta(Fe-Si)$ , and  $\beta(Mn-Si)$ .

### The Liquidus (Aluminium Corner)

Just as in a ternary system the primary phase fields and their intersections—the binary valleys and invariant

points—can be represented by a two-dimensional diagram, which is the projection of the liquidus surface on the base of the three-dimensional model, so in a quaternary system the liquidus can be represented by a three-dimensional model, usually a tetrahedron, of which the faces are the basal projections of the liquidus surfaces of the four constituent ternary systems. In such a model, the separation of the primary constituent is represented by a volume; of two constituents simultaneously by a surface; of three, by a line; of four, by a point. Isothermals can, if desired, be inserted.

The liquidus model for the aluminium corner of the quaternary system is shown, in clinographic projection, in Fig. 3. The eye of the observer is supposed to be at an infinite distance, so that parallel lines remain parallel in the drawing, and is also supposed to be above and slightly to the right of the centre of the model, so that the upper and right-hand surfaces are visible. Isothermals would add to the complexity of the diagram and have not been inserted. The base of the model is the basal projection of the liquidus of the aluminium-silicon-iron system, the front is that of the aluminium-manganese-silicon system, and the left-hand end is that of the aluminium-manganese-iron system.

If the amount of one of the components of a quaternary system is maintained constant, the resultant series of alloys may be treated as ternary system, and its constitution represented by a three-dimensional model. Its liquidus may then be represented in the usual way by a two-dimensional diagram which, for convenience, may be designated a "pseudo-ternary" liquidus diagram. Three such diagrams form the top-back, and right-hand

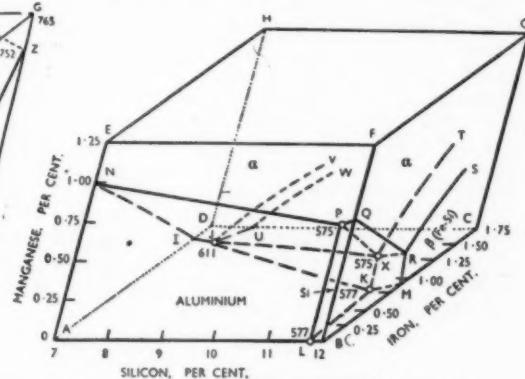


Fig. 4.—The liquidus: Silicon-rich alloys.

end of the model of Fig. 3 and are, respectively, those of alloy series containing 4% manganese, 4% iron, and 4% silicon.

In the range of compositions covered by Fig. 3 there are six primary phase fields or regions, five of them extending to the front face of the model, and the sixth lying towards the back. The primary constituents have been indicated in the diagram: the names are supposed to have been written on the front, top, and left-hand faces of the model. Some of the surfaces separating these primary regions are eutectic surfaces, others are associated with peritectic reactions. A list of them is given in Table III.

The intersections of these binary surfaces are lines which represent the simultaneous presence of three solid phases and liquid, and are therefore univariant,

<sup>6</sup> V. Fuss, *Z. Metallkunde*, 1931, **23**, 231.

F. Nishimura, *Mem. Coll. Eng. Kyoto Imp. Univ.*, 1933, **7**, 285.  
G. Urasawa and A. N. Sushina, *Metalurgia*, 1937, (4), 27.

L. N. Sergeev and B. I. Rimmer. *Metallurg*, 1937, (9).

W. Jänicke, *Aluminium-Archiv*, 1936, (5)

Four of these univariant lines meet at each of the invariant points  $\theta$ ,  $\phi$ , and  $\psi$ .

TABLE III.  
BINARY SEPARATIONS.

Phase Boundary.	Letters, Fig. 3.	Nature of Binary Surface.
Aluminiun— $\text{MnAl}_4$	KL $\psi$ S	Eutectic complex: $\text{Al} + \text{MnAl}_4$
" " $\alpha$	LRJ $\psi$	" " $\text{Al} + \alpha$
" " $\text{FeAl}_3$	SIJ $\psi$	" " $\text{Al} + \text{FeAl}_3$
$\text{MnAl}_4$ — $\text{FeAl}_3$	T $\phi$ PS	Peritectic: $\text{Liq.} + \text{MnAl}_4 \rightarrow \text{FeAl}_3$
" " $\alpha$	O $\phi$ PS	Peritectic: $\text{Liq.} + \text{MnAl}_4 \rightarrow \alpha$
$\text{MnAl}_4$ — $\text{MnAl}_6$	MN $\theta$ T	Peritectic: $\text{Liq.} + \text{MnAl}_6 \rightarrow \text{MnAl}_4$
" " $\text{FeAl}_3$	UV $\theta$ T	Eutectic complex: $\text{MnAl}_4 + \text{FeAl}_3$
" " $\beta(\text{Mn-Si})$	PN $\phi$ V	Eutectic complex: $\text{MnAl}_4 + \beta(\text{Mn-Si})$
$\beta(\text{Mn-Si})$ — $\text{MnAl}_6$	NO $\phi$ θ	Peritectic: $\text{Liq.} + \beta(\text{Mn-Si}) \rightarrow \text{MnAl}_6$
" " $\alpha$	OQY $\psi$ W $\phi$	Eutectic: $\beta(\text{Mn-Si}) + \text{FeAl}_3$
$\text{FeAl}_3$ — $\alpha$	V $\phi$ W $\psi$ ZX	Peritectic: $\text{Liq.} + \text{FeAl}_3 \rightarrow \alpha$

To construct the liquidus model, pseudo-ternary liquidus diagrams were drawn parallel to the three faces, at intervals of 0.5%. Phase boundaries and isothermals were plotted from examination of microsections and from the primary arrest temperatures, and were adjusted so as to give smooth curves consistent in the three sets of diagrams. One set of these diagrams, representing alloys with constant manganese content, is reproduced in the original paper.

It is shown that all the alloys in the range of compositions covered by Fig. 3 solidify in such a way that the points representing the composition of the liquid eventually reach the aluminium— $\alpha$  surface—or lie below it: their loci leave the model, move to the right, through the line RJ, or through the triangle BRJ. To follow the concluding stages of solidification, it is therefore necessary to know something about that part of the primary aluminium phase field and its boundaries which lie to the right of Fig. 3. A few experiments sufficed to show that between 4 and 7.5% silicon the only surface bounding the primary aluminium field was that due to the aluminium— $\alpha$  separation; this surface gradually approached the aluminium-silicon axis of the model as the silicon content increased. With more than 7.5% silicon, new surfaces, due to aluminium— $\beta(\text{Fe-Si})$  and aluminium-silicon made their appearance, and a more detailed study was necessary.

### The Liquidus-Silicon-Rich-Alloys

A liquidus model, covering the limited range studied, is shown in clinographic projection and reproduced in Fig. 4. The aluminium— $\alpha$  boundary surface, which leaves Fig. 3 through the line RJ, enters Fig. 4 through the line NI, and continues as far as the lines JX, XP. Aluminium is primary below this surface, and its phase field is bounded at the back by the aluminium— $\beta(\text{Fe-Si})$  surface JKX, and on the right-hand side by the aluminium-silicon surface PLKX. Letters indicating the various primary fields have been inserted in the diagram and are supposed to have been written on the front and exposed end of the model. No attempt was made to explore the primary  $\beta(\text{Fe-Si})$  field or the adjacent one due to primary silicon; only the boundaries with the aluminium field were studied in detail. The position of the invariant point X was found by constructing a pseudo-ternary diagram for alloys containing 11.7% silicon; its temperature, as far as could be ascertained,

was identical with that of the aluminium— $\alpha$ -silicon invariant point P, 575°C.

Particulars of the binary, ternary, and quaternary invariant points in the range covered by Fig. 4 are given in Table V.

TABLE V.  
BINARY, TERNARY, AND QUATERNARY INVARIANT POINTS:  
SILICON-RICH ALLOYS.

Invariant Point.	Nature.	Solid Phases Present.	Composition, %.			Temp., °C.
			Mn	Si	Fe	
J	Peritectic	$\text{Al}, \alpha, \beta(\text{Fe-Si})$	—	7.5	1.5	611
K	Ternary eutectic	$\text{Al}, \beta(\text{Fe-Si}), \text{Si}$	—	11.6	0.8	577
L	Binary eutectic	$\text{Al}, \text{Si}$	—	11.77	—	577
P	Ternary eutectic	$\text{Al}, \alpha, \text{Si}$	0.75	11.75	—	575
X	Peritectic	$\text{Al}, \alpha, \beta(\text{Fe-Si}), \text{Si}$	0.2	11.7	0.6	575

### Secondary Separations

A model representing the secondary fields at the aluminium corner of the quaternary system is reproduced in Fig. 5. In this diagram the formulae identifying the binary surfaces have been inserted, and are supposed

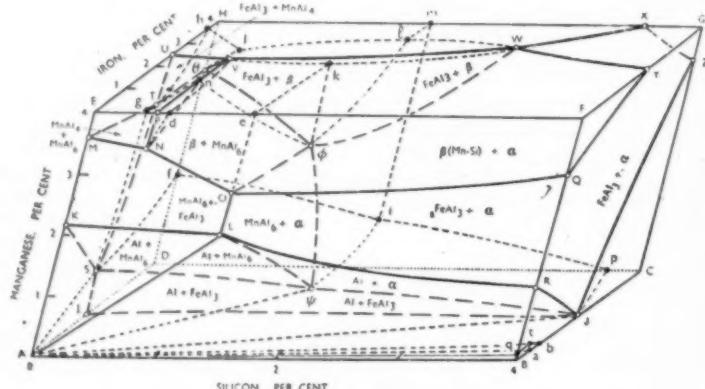


Fig. 5.—Secondary separation: General view.

○ Points associated with primary boundaries.  
● Points associated only with secondary boundaries.

to have been written on the parts of the surfaces visible to the eye.

Alloys of which the primary constituent is aluminium can be divided into five groups, according to the identity of the secondary constituent. In this region, the loci of points representing the change in liquid composition during the primary separation are lines which are almost straight and which radiate from the aluminium corner. The range of compositions within which  $\text{MnAl}_4$  is secondary is therefore indicated in Fig. 5 by a four-sided pyramid of which the base is the surface  $\text{KL}\psi\text{S}$  and the apex the aluminium corner. Similarly, the range within which  $\text{FeAl}_3$  is secondary is represented by a pyramid of which the base is the surface  $\text{SIJ}\psi$ . Only a part of the aluminium— $\alpha$  secondary region lies within the confines of Fig. 5; it occupies the greater part of the volume below the surface  $\text{RJ}\psi$ , and its intersection with the right-hand face of the model is the area  $\text{RJ}\psi\text{tq}$ . The high-silicon end of the aluminium— $\alpha$  region is shown in another diagram (not reproduced).

Other regions are briefly described, in which the primary constituent is  $\text{MnAl}_4$  or  $\text{MnAl}_6$ ,  $\beta(\text{Mn-Si})$ , or  $\text{FeAl}_3$ . Ternary and later separations are discussed.

(Continued on page 224)

# Present Position of Field Tests on Atmospheric Corrosion

## The Work of the Corrosion Committee of the Iron and Steel Institute

By J. C. Hudson, D.Sc.

*Information is given concerning atmospheric corrosion tests made on ordinary ferrous materials of construction, including wrought irons, ingot irons, and steels both of ordinary and of low-alloy type. The main tests were made at fourteen stations, representing marine, rural, industrial, tropical and arctic conditions. Some of the results are abstracted and given in this article, together with the author's conclusions.*

THIS report<sup>1</sup> brings up to date the results of the main corrosion tests on specimens of various irons and steels exposed to the atmosphere in the bare condition that the author is conducting on behalf of the Corrosion Committee. Earlier reports on this long-range investigation are published in the Committee's Reports.<sup>2</sup>

The programme has involved tests at fourteen exposure stations, seven at home and seven overseas (Table I), and the materials tested include mild steel, various types of wrought iron, ingot iron, Aston-Byers' iron, and various low-alloy steels (Table II). All the materials are commercial products; in the great majority of cases their production was witnessed, and full details of the procedure followed, analyses, mechanical properties, etc., are recorded. The standard size of specimen is  $15 \times 10 \times \frac{3}{8}$  in. (in a few cases the thickness varied from  $\frac{3}{8}$  in.), either rolled as flats or cut from plates. The surface condition before exposure was varied, as indicated in Table III. All specimens were weighed before test, and were hung vertically on steel stands, freely exposed to the air. Duplicates of each material were placed in different rows, to minimise any effect due to the different height from the ground.

The standard exposure period is five years, but in some cases, notably at Sheffield and Llanwrtyd Wells, one- and two-year tests have been made on similar sets of materials, and two additional sets will be exposed for longer periods (ten years and more), to determine how the rate of corrosion varies with time. A few tests over shorter periods have been made for other purposes.

All specimens are inspected at intervals, the chief observations being the extent to which the mill scale has been shed from as-rolled specimens and the colour and type of the rust on the various materials.

After exposure, the specimens are examined and weighed, both as received in the laboratory and after removal of the rust, which is effected in two stages. From the final weighing the loss in weight is determined, minor corrections being applied for slight differences in surface area. Since, with few exceptions, no marked pitting has been observed in these tests, the losses in weight may be taken as a true index of the relative resistance to corrosion of the various materials.

A total of 1,054 specimens has been exposed during the course of this research. Tests have now been completed on 856, and the results given are means of two specimens. In the great majority of cases the duplicates agreed within 5%. Where applicable, the rate of corrosion is expressed in thousandths of an inch (mils.) of metal per year—i.e., the thickness of the layer of metal destroyed by rusting in the course of a year. Comparisons of dissimilar materials are made by reference to the standard reference material, ordinary low-copper mild steel X, which was included in all test series; the relative corrosion of this material is taken as 100.

The data thus accumulated permit of authoritative answers to the following questions:—

1. What is the effect of different types of atmosphere on the rate of rusting of ordinary mild steel?
2. What is the rate, and how does it vary with the duration of exposure?
3. To what extent does the resistance of mild steel to atmospheric corrosion differ from that of wrought iron or ingot iron?

TABLE I.—PARTICULARS OF THE CORROSION STATIONS.

Station.	Type of Atmosphere.	Mean Annual Temp., °F.	Rainfall, In.	Relative Humidity, %	Overseas.						
					Station.	Type of Atmosphere.	Position.		Temp., °F.	Rainfall, In.	Relative Humidity, %
							Lat. °	Long. °			
Calshot	Marine	51	26	84	Abisko, Sweden	Sub-polar	68 N.	19 E.	30	11	74
Dove Holes Tunnel	Railway tunnel	—	—	—	Apapa, Nigeria	Marine-tropical	7 N.	4 E.	80	72	79
Llanwrtyd Wells	Rural	47	55	79	Aro, Nigeria	Inland-tropical	7 N.	3 E.	77	45	84
Moatmoorwell	Industrial	48	32	82	Basrah	Dry sub-tropical	31 N.	48 E.	75	7	64
Leeds	Marine-industrial	48	25	84	Congella, South Africa	Marine	30 S.	31 E.	71	43	76
Sheffield	Industrial	48	30	84	Khartoum	Dry tropical	16 N.	33 E.	85	6	31
Wolverhampton	Industrial	50	23	81	Singapore	Marine-tropical	2 N.	104 E.	81	95	80

TABLE II.—PARTICULARS OF THE MATERIALS TESTED.

Designation.	Analysis.						Mechanical Properties.		
	C, %	Cr, %	Cu, %	Mn, %	P, %	Si, %	Yield-point Tons per Sq. In.	Max. Stress, Tons per Sq. In.	Elongation on 2 in., %
<b>Steels.<sup>3</sup></b>									
K	0.25	0.98	0.03	0.60	0.04	0.12	25	39	27.8
L	0.25	0.59	0.48	0.58	0.03	0.13	24	37	29.5
M	0.27	0.60	0.50	0.89	0.04	0.15	27	41	25.0
N	0.26	0.95	0.48	0.84	0.05	0.13	31	46	20.5
O	0.23	0.03	0.52	1.56	0.04	0.33	29	43	23.5
P <sup>4</sup>	0.17	—	0.05	0.55	0.04	0.06	—	—	—
Q <sup>4</sup>	0.14	—	0.10	0.56	0.04	0.09	—	—	—
W <sup>5</sup>	0.03	Nil	0.04	0.03	0.01	0.03	12	21	41.8
X	0.20	Nil	0.02	0.59	0.04	0.02	18	30	31.7
X2	0.24	0.04	0.02	0.57	0.04	0.02	18	30	33.8
XK	0.21	0.07	0.03	0.5	0.04	0.10	20	31	30.8
Y	0.21	Nil	0.22	0.59	0.04	0.03	19	31	32.3
Z	0.21	Nil	0.48	0.61	0.04	0.03	18	32	29.1
ZK	0.23	0.05	0.50	0.60	0.03	0.12	21	33	32.3
<b>Wrought Irons:</b>									
H Aston-Byers	0.02	Trace	Trace	0.02	0.11	0.13	13	18	13.3
R Swedish	0.03	Nil	Trace	Nil	0.05	0.02	13	20	29.3
S Swedish	0.02	Nil	0.60	Nil	0.05	0.02	15	22	26.3
T Staffordshire	0.03	Trace	0.04	0.02	0.24	0.14	15	22	17.0
T <sup>2</sup> Staffordshire <sup>6</sup>	0.02	0.01	0.07	0.01	0.32	0.13	16	21	12.4
V Scottish	0.03	Nil	0.12	0.03	0.17	0.16	15	21	14.6

<sup>1</sup> Mean values for transverse and longitudinal tests.<sup>2</sup> Particulars of other steels from the Institute of Welding, etc., tested in one series only are given in Table XIII.<sup>3</sup> 0.13% As, 0.05% S.<sup>4</sup> 0.12% As, 0.04% S.<sup>5</sup> Ingot iron.<sup>6</sup> A "repeat" batch of wrought iron T.TABLE III.  
PARTICULARS OF SURFACE TREATMENTS BEFORE EXPOSURE.<sup>7</sup>

With Mill Scale.	Without Mill Scale.
r. <i>As-rolled</i> .—Materials prepared by the normal hot-rolling process, kept as free from rust as possible, and cleaned with carbon tetrachloride before exposure.	p. <i>Pickled</i> .—In 15% by volume sulphuric acid at 40°C. Approximate time required 30 mins.
r1. <i>As-rolled, reduced rolling temperature</i> .—As (r) but rolling completed at a reduced rolling temperature. With some materials ( <i>cf.</i> Third Report, loc. cit., p. 68) different methods of obtaining a low-temperature finish were compared.	s. <i>Sand-blasted</i> . <sup>8</sup> —Air pressure 12 lb. per sq. in.; distance from nozzle 3-6 in. Leighton Buzzard sand.
r2. <i>As-rolled, alternative rolling temperature</i> .—As (r), but rolling not conducted normally, the material usually being finished at a higher temperature than normal.	m. <i>Machined</i> .—Depth of cut $\frac{1}{8}$ in. transverse $\frac{1}{4}$ in.; cutting speed 60 ft. per min.; done dry.
	pol. <i>Polished</i> .—Buffed to a mirror finish in 7 stages: (1) Ground on stone, (2) 60-grade emery, (3) 90-grade emery, (4) 140-grade emery (5) emery compo, (6) Tripolicompo, (7) Chrome compo. Peripheral speed of wheel about 6,000 ft. per min. for stages (1) and (2) and 7,500 ft. per min. for finishing stages.

<sup>7</sup> For further details see First Report, loc. cit., p. 67.<sup>8</sup> Sand-blasting was used for the earliest series of tests, as described. In later series shot-blasting has been substituted. The two processes may be regarded as equivalent for the present purpose.

- What is the effect of the addition of low percentages of alloying elements on the rate of atmospheric corrosion of mild steel?
- What is the effect, if any, of the initial surface condition?
- What length of exposure is needed to remove the mill scale from as-rolled iron or steel by natural weathering?
- What are the effects of sundry variables (the method of piling wrought iron; different conditions of test exposure)?
- What protection is afforded to steel by galvanised coatings?

The questions are discussed in sections under their respective heading, but it is only possible here to give the author's main conclusions resulting from the tests.

#### Effect of Climate on the Rates of Atmospheric Corrosion

The effect of different climates on the rate of atmospheric corrosion of ordinary irons and steels is best illustrated by the data summarised in Table IV. These are the figures in mils. per year calculated from observed

losses in weight of specimens of the standard reference steel, mild steel X, containing 0.2% of carbon, 0.6% of manganese, and no added copper (actually 0.02%). Values are available for all fourteen stations, in some cases for two or even three series of tests. The reproducibility from one test series to another at the same station is good.

From the results and the discussion, the author states, it may be concluded that, as a rule, straightforward corrosion of iron and steel should not be marked in non-industrial, tropical or sub-polar climates, and that the primary cause of severe corrosion is industrial pollution. Unfortunately, this conclusion is not so reassuring as it sounds, for two reasons:—

(a) The fact that iron or steel is used at all at the places concerned will often imply that there is at least some industrial activity there; and

(b) Corrosion may not be straightforward.

The first point is obvious; while after an examination of the second the author concludes that:—

(i) In certain climates, particularly where the relative humidity or the temperature is low, it may be unnecessary to protect steel at all, provided that there is no danger of local attack being promoted by the formation of scaly rust. This will largely depend on the form in which the steel is used and on local conditions; the best ultimate criterion will be experience gained from the behaviour of similar structures in the past. For instance, in certain parts of Nigeria it should be possible to use ordinary black corrugated sheets for roofing without protecting them against corrosion.<sup>9</sup> On the other hand, near the coast the presence of salt spray in the air may be found to produce the scaly-rust type of attack, and painting may be necessary; this may even depend on the pitch of the roof.

(ii) Thick rust should never be allowed to accumulate on iron or steel. A thin uniform fine layer of rust may not be harmful, but rust of the scaly type is deadly.

#### Variation in the Rate of Atmospheric Corrosion of Mild Steel with Time

Three series of tests at Sheffield and a fourth made at Llanwrtyd Wells supply information on this point. In

<sup>9</sup> Temperature effects inside a building are another matter.

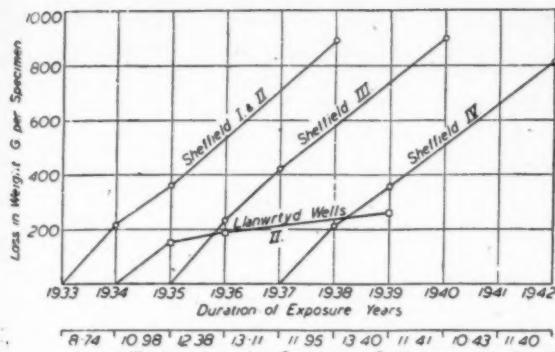


Fig. 1.—Variation in corrosion of mild steel X with time.

each case similar sets of specimens were exposed simultaneously and removed, respectively, after one, two and five years' exposure. The ordinary standard mild steel X was included in all sets, and the corrosion rates observed for this material are given in Table V. The losses in weight of the specimens are plotted in Fig. 1, beneath which are shown values for the losses in the weight of ingot-iron pollution specimens which were exposed for periods of twelve months throughout the test periods. The latter are a rough index of annual variations in the corrosiveness of the atmosphere, due to changing meteorological and industrial factors.

It is concluded that in the absence of complicating factors, such as the formation of scaly rust, the corrosion of ordinary steel in the atmosphere is at worst directly proportional to the duration of exposure and may in practice prove less than this. Although the data presented here are limited to ordinary steel, this conclusion is broadly tenable, on the basis of the experimental results, for all other wrought irons or low-alloy steels tested.

#### Comparative Resistance of Mild Steel, Wrought Iron, Ingot Iron and Aston-Byers' Iron to Atmospheric Corrosion

**Wrought Iron.**—There is a sharp distinction between the behaviour of wrought irons produced from relatively impure ores, with high-silicon and phosphorus contents, and those produced from high-grade ores of Swedish or other origin. The essential difference between them lies in their slag content; as is reflected in the analyses

for phosphorus and silicon, shown in Table II, this is much higher in the British than in the Swedish wrought iron.

The experimental fact, which is demonstrated by the results grouped in Tables VI and VII, is that the less pure British wrought irons have a superior corrosion resistance to that of ordinary mild steel, whereas the very pure Swedish iron is markedly inferior to the latter material. In round figures, taking the corrosion of mild steel as 100, the margins in favour of the British wrought irons, or to the disadvantage of the Swedish material may both be assessed at 25%.

Three factors are discussed—mill scale, mechanical obstruction by slag particles, and the phosphorus content—to which the superiority of the less pure wrought irons as compared with mild steels may be attributed, but on the whole the effect of the phosphorus content is probably the most important.

**Ingot Iron.**—There is no evidence whatever that the resistance to atmospheric corrosion of ingot iron, which is essentially a dead mild steel, in which the carbon, manganese, phosphorus, silicon and sulphur contents have been reduced to the lowest practicable limits, is superior to mild steel itself. Indeed, if anything, over long periods of exposure the advantage lies with mild steel.

**Aston-Byers' Iron.**—This is a synthetic wrought iron made by a special process, which consists of pouring dead mild steel, made by the acid Bessemer process, into a bath of molten synthetic slag. The resulting mass of metal and slag is pressed into a bloom, which can be worked by rolling and piling in the same way as ordinary wrought iron.

The results of tests over five years show that this iron proved approximately 10% more corrodible than mild steel itself, whereas in these particular tests Staffordshire wrought iron lost from 25 to 36% less weight than mild steel. Hence, as regards atmospheric corrosion resistance,

TABLE V.  
VARIATION IN CORROSION RATE OF MILD STEEL WITH TIME.  
Specimen exposed with mill scale.

Station.	Test Series.	Loss in Weight G. per Specimen.			Corrosion Rate, Mils. per Year.		
		1 Year.	2 Years.	5 Years.	1 Year.	2 Years.	5 Years.
Llanwrtyd Wells	II	150	189	260	3.63	2.29	1.26
Sheffield	I and II	214	359	889	5.18	4.35	4.30
	II	229	420	900	5.54	5.08	4.36
	IV	211	360	817	5.11	4.36	3.96

TABLE IV.—RATE OF CORROSION OF MILD STEEL OVER A FIVE-YEAR PERIOD.  
Specimens exposed with mill scale.

Home.				Overseas.			
Station.	Test Series.	Mils per Year	Relative to Sheffield (= 100)	Station.	Test Series.	Mils per Year	Relative to Sheffield (= 100)
Culshot	I. & II.	1.62	38	Abisko <sup>1</sup>	I. & II.	0.27	6
Blue Holes Tunnel	I.	2.39	57	Apapa	I.	0.77	18
Llanwrtyd Wells	II.	2.29	54	Aro <sup>2</sup>	I.	0.45	11
	I.	1.22	29	Basrah	I.	0.46	11
Motherwell	II.	1.26	30	Congella	I.	1.82	43
Scunthorpe	I.	2.15	51	Khartoum	III.	1.85	44
Sheffield	I.	1.92	46		I.	0.034	1
	I. & II.	4.30	102		II.	0.034	1
	III.	4.36	104	Singapore <sup>1</sup>	I.	0.62	15
	IV.	3.96	94		II.	0.53	13
Woolwich	I.	2.26	54				

<sup>1</sup> Owing to the outbreak of war, it was decided to continue the exposure of test series III. at Abisko and Singapore beyond 5 years. The Singapore specimens have since been presumed lost.

<sup>2</sup> 80% of the mill scale was intact after exposure.

TABLE VI.—COMPARISON OF MILD STEEL, COPPER-BEARING STEEL, WROUGHT IRON AND INGOT IRON.  
Specimens exposed with mill scale.

Station.	Duration of Test, Years.	Corrosion Rate of Steel X <sup>1</sup> , (Cu 0.02%), Mils per year.	Relative Corrosion (Mild Steel X = 100).						
			Wrought Irons.				Ingot Iron W.	Mild Steels.	
			R. Swedish.	S. Swedish (Cu 0.6%),	T. Staffordshire,	V. Scottish.		Y (Cu 0.2%),	Z (Cu 0.5%).
Abisko	5	0.27	—	(See footnote No. 1)	113	102	148	81	78
Calshot	5	1.62	—	92	78	90	96	—	—
Dove Holes Tunnel	5	2.29	98	—	—	—	—	—	—
Khartoum	5	0.03	(See footnote No. 1)	—	—	—	—	—	—
Llanwrtyd Wells	1	3.63	—	77	— <sup>2</sup>	— <sup>2</sup>	89	66	70
	2	2.29	111	83	88	86	93	72	74
	5	1.26	111	89	78	83	110	84	84
Sheffield	1	5.18	—	82	—	—	88	78	77
	2	4.35	150	75	73	70	93	79	77
	5	4.30	155	68	77	73	104	80	79
Singapore	5	0.53	—	—	77 <sup>2</sup>	41 <sup>2</sup>	101	—	—

<sup>1</sup>The losses in weight of the specimens at Abisko and Khartoum were so small that no comparison of materials is warranted.<sup>2</sup>These specimens were incompletely descaled at the end of the test.

this iron is to be classed with ordinary steels rather than with wrought irons.

#### Effect of Low Percentages of Alloying Elements on the Resistance of Iron and Steel to Atmospheric Corrosion

The conclusions to be drawn concerning the effect of low percentages of alloying elements on the resistance of iron and steel to atmospheric corrosion are based in the main on two distinct series of experimental results. In general, these results show that it is possible by the addition of small quantities of suitable alloying elements to ordinary mild steel to produce structural steels of which the resistance to atmospheric corrosion is up to twice as great as that of the unalloyed steel. Since the improvement in corrosion resistance is accompanied by an enhancement of mechanical properties of corresponding magnitude and since these improvements are obtained at a remunerative cost in terms of the alloying elements used, there should be a wide field of usefulness for such steels.

*Effect of Copper.*—The Committee's tests have fully confirmed the pioneer work of the American Society for

Testing Materials, and individual American investigators, which led to the recognition of the beneficial effect of a small percentage of copper in iron or steel on its resistance to atmospheric attack. From the data given in Table VI the following generalisation seems justified:—

The addition of low percentages of copper to mild steel has the effect of improving the resistance of this material to atmospheric corrosion to a degree which renders this comparable with that of unalloyed British wrought irons. It may be added that the results of atmospheric corrosion tests on wires<sup>4</sup> show that the effect of adding small percentages of copper alone to British wrought iron renders the corrosion resistance of this material comparable with that of mild steel containing both copper and chromium.

*Effect of Chromium.*—The effect of the presence of small quantities of chromium in steel is illustrated by the data given for steel K in Table XI. This steel differs from the standard unalloyed steel X<sup>2</sup><sup>5</sup> in containing 1.0% of chromium; its loss in weight after five years' exposure at Congella or Sheffield was approximately 60% of that of the standard steel. Hence the addition of even a low percentage of chromium to steel improves its resistance to atmospheric corrosion considerably.

*Joint Effect of Copper and Chromium.*—Reference to Table XI shows that, whilst the effects of copper and chromium when present simultaneously are supplementary, they are not fully additive. Three distinct copper-chromium steels were tested, L, M and N; each contains 0.5% of copper, but the chromium content is 0.6% for L and M and 1.0% for N. There is a difference

COMPARISON OF ASTON-BYERS IRON, WROUGHT IRON, MILD STEEL AND COPPER-CHROMIUM STEEL AT SHEFFIELD. (PART IV.)

Duration of Test, Years.	Surface Condition,	Corrosion Rate of Steel X <sup>2</sup> , Mils per Year.	Relative Corrosion.			
			Aston-Byers Iron H/AB.	Wrought Iron T <sup>2</sup> .	Mild Steel X <sup>2</sup> .	Steel N (Cr 1.0%, Cu 0.5%).
1	Sand-blasted	4.53	114	75	100	62
		5.11	99	67	100	70
2	As-rolled	4.36	103	64	100	—
		3.96	103	64	100	40

<sup>4</sup> Fifth Report, *loc. cit.*, p. 260, and further unpublished data.<sup>5</sup> A repeat cast identical with steel X, as shown by metallurgical examination and test data (cf. footnote to Table XI).

TABLE XI.—EFFECT OF COPPER AND OR CHROMIUM ADDITIONS ON THE ATMOSPHERIC CORROSION OF MILD STEEL. COMPARISON WITH COPPER-BEARING SWEDISH WROUGHT IRON.

Specimens exposed with mill scale.

Station, <sup>1</sup>	Duration of Test Years.	Corrosion Rate of Steel X <sup>2</sup> , Mils per Year.	Relative Corrosion.								
			Steels.								
			K (Cr 1.0%),	L (Cr 0.6%, Cu 0.5%),	M (Cr 0.6%, Cu 0.5%),	N (Cr 1.0%, Cu 0.5%),	O (Mn 1.6%, Cu 0.5%),	X <sup>2</sup> (Cu 0.02%, Si 0.02%),	XX (Cu 0.02%, Si 0.10%),	ZK (Cu 0.5%),	Wrought Iron S (Cu 0.6%).
Congella	5	1.85	62	61	62	54	69	100 <sup>2</sup>	89	74	83
Sheffield	1	5.27	—	—	—	75	—	100	—	78	—
	1	5.54	73	68	70	67	67	100	89	63	84
	2	5.08	73	68	67	60	73	100	89	71	76
	5	4.36	60	61	58	46	78	100	89	78	65

<sup>1</sup> No data are available for the series at Abisko and Singapore. See footnote No. 1 to Table IV.<sup>2</sup> Loss in weight of steel X<sup>2</sup>, 217.5; of steel X, 218.

TABLE XIII.—COMPARISON OF VARIOUS COMMERCIAL LOW-ALLOY STEELS FROM THE INSTITUTE OF WELDING, ETC.  
All specimens shot-blasted before exposure. Duration and place of test, one year at Sheffield.

Steel. Reference and Type.	Analysis.							Relative Corroborability (Steel X2 = 100). <sup>2</sup>
	C, %	Mn, %	Si, %	Cr, %	Cu, %	Ni, %	Other Elements, %	
WE 3% nickel	0.51	0.59	0.22	0.10	0.09	3.12	—	43
WN Nickel-copper (low-carbon)	0.09	0.38	0.14	0.03	0.95	1.96	—	56
WP Nickel-copper (high-carbon)	0.20	0.70	0.17	0.04	1.05	1.93	—	56
WD 2% nickel	0.20	0.68	0.11	0.01	0.05	2.44	—	59
WL Cu-Ni-Mo	0.07	0.60	0.03	0.04	1.13	1.31	Mo 0.10	60
WF Cr-Cu-Si-P	0.08	0.28	0.46	0.82	0.40	0.04	P 0.15	61
WG Cr-Mn-Cu	0.18	0.82	0.07	0.83	0.31	0.03	—	65
DN Copper-chromium <sup>3</sup>	0.25	0.84	0.05	0.90	0.33	0.03	—	66
WK Cu-Cr-Si-Zr	0.11	0.55	0.78	0.45	0.16	0.09	Zr 0.10	66
ZKF Copper-manganese <sup>3</sup>	0.19	1.34	0.21	0.08	0.44	0.01	P 0.05, S 0.05	70
WB Copper-manganese	0.21	1.41	0.09	0.07	0.52	0.07	P 0.06, As 0.05	74
YF 0.35% copper <sup>3</sup>	0.17	0.56	0.03	0.04	0.35	0.01	—	76
DX Mild <sup>3</sup>	0.19	0.46	0.02	0.02	0.07	0.04	—	92
WC Admiralty D	0.24	1.40	0.06	0.03	0.04	0.07	As 0.11	95
WA Carbon-manganese	0.19	1.54	0.09	0.08	0.03	0.04	S 0.05, As 0.05	97
X2 Corrosion Committee's standard mild steel	0.24	0.57	0.02	0.04	0.02	—	—	100

<sup>1</sup> Present in amounts of 0.05% or more.<sup>2</sup> The loss in weight of steel X2 was equivalent to an annual corrosion rate of 4.51 mils.<sup>3</sup> Included in the coal-wagon tests of the Sub-Committee on Low-Alloy Steels.

too in manganese content, which is 0.6% for L, but 0.8-0.9% for M and N. Comparison of the results for these steels amongst themselves and with those for steel K (1.0% of chromium, but no added copper) and ZK (0.5% of copper, but no added chromium) shows that:

(i) The optimum corrosion resistance is obtained, as might be expected, in the most highly alloyed material, steel N, with 0.5% of copper, 1.0% of chromium, and 0.8% of manganese. (The effect of manganese will be discussed later.)

(ii) Steels L and M, containing 0.6% of chromium with 0.5% of copper, are roughly equivalent to steel K, which contains 1.0% of chromium alone.

(iii) The resistance of steel N over five years' exposure is approximately double that of the unalloyed basis steel, X2.

**Effect of Silicon.**—The series of steels prepared for test by the Committee were not specifically intended to study the influence of silicon on the resistance of steel to atmospheric corrosion, but despite this, some interesting indications can be drawn as to its probable effect. For instance, steels X2 and XK (Table XI) differ only in that the former contains 0.02% of silicon and the latter 0.10% (Table II); in steelmaking parlance, the first steel is "balanced," the second "semi-killed." The experimental fact is that XK has corroded 11% less than X2. To sort out the effect of each individual element, however, appropriate variation in analysis would be needed, and arrangements for such tests are in hand. Meanwhile, it may tentatively be concluded that the addition to steel of small amounts of silicon (and possibly of other deoxidising elements) will have a generally beneficial effect in increasing the resistance to atmospheric corrosion.

**Effect of Manganese.**—The only clear-cut comparison relating to the effect of manganese is the relative behaviour of steels L and M. Both steels contain 0.6% of chromium and 0.5% of copper, but steel L has 0.58% and steel M 0.89% of manganese (Table II). In the atmospheric corrosion tests (Table XI) there was no significant difference between them.

**Effect of Arsenic.**—Some indication of the effect of this element on resistance to atmospheric corrosion is given by the results obtained for two steels P and Q (Table II), taken from steelworks' stock. Reference to Table XII shows that steel Q, which contains 0.10% of copper, is equal or superior to steel Y, containing 0.22% of copper. Since, in addition, steel P, with 0.13%

TABLE XII  
EFFECT OF ARSENIC CONTENT ON THE ATMOSPHERIC CORROSION OF MILD STEEL.  
Specimens exposed with mill scale.

Station.	Duration of Test Years.	Corrosion Rate of Steel X (As 0.05%, Cu 0.02%), Mils per Year.	Relative Corrosion.		
			Steel P (As 0.13%, Cu 0.05%),	Steel Q (As 0.12%, Cu 0.10%),	Steel Y (As 0.05%, Cu 0.22%),
Khartoum	5	0.05 <sup>1</sup>	—	—	—
Sheffield	5	4.30	92	81	80
Singapore	5	0.53	83	70	—
Llanwryd Wells	5	1.26	—	74	84

<sup>1</sup> The corrosion rate is too small to warrant any comparison between the different steels, which were only partially descaled after 5 years' exposure.

of arsenic and 0.05% of copper, is distinctly superior to the standard low-copper steel, it may be concluded that the presence of small percentages of arsenic in steel increases its resistance to atmospheric corrosion.

**Effect of Nickel and Other Elements.**—The results of tests on sand-blasted specimens exposed for one year are given in Table XIII. The steels are arranged in order of merit, and, in conformity with other tables, their losses in weight are expressed as a percentage of that of the standard mild steel X2. Four nickel or nickel-copper steels head the list and another occupies the sixth position. It is probable that the corrosion resistance increases with the nickel content, since the best steel of all, WE, contains the highest amount of this element, 3.12%; this steel is approximately twice as resistant as the unalloyed standard steel X2. It is also apparent that the effects of copper and nickel reinforce each other.

The chromium-copper-silicon-phosphorus steel WH occupies a high position in the order of merit and has proved superior to the plain copper-chromium steels WG and DN; this is probably attributable to the higher silicon and phosphorus contents of steel WH, as already mentioned.

#### Effect of the Initial Surface Condition

The surface condition of the specimens prior to exposure was varied in many cases (Table III), since it was thought possible that this might have some effect on the results obtained. From these results it may be briefly stated that:

(i) Although the surface condition of the specimen may play a part in retarding the initiation of atmospheric corrosion—for instance, mill scale or the adherent sand

deposit left after sand-blasting may do so—such effects are generally transient and become relatively unimportant over long periods of exposure in corrosive atmospheres.<sup>6</sup>

(ii) There is no evidence—again with reference to long periods of exposure and corrosive atmospheres—that the order of resistance of different materials to atmospheric corrosion is appreciably affected by differences in their surface condition before exposure, provided that this surface condition is the same for all.

#### Time Necessary to Remove Mill Scale from Steel by Weathering in the Atmosphere

From the results as a whole no marked difference was observed in the rates of descaling of ordinary and of copper-bearing steels. There was no evidence that the presence of copper in steel retards the rate at which it sheds its mill scale. If anything, the copper-bearing steels were descaled more rapidly than the ordinary steel, which would agree with the fact that the mill scale was thinner on the former. (At least, as judged by the average losses in weight on sand-blasting numerous specimens of each type.)

#### Effect of Sundry Variables

The effect of the method of piling wrought iron and different conditions of exposure are discussed under this

<sup>6</sup> In this connection, by "corrosive atmospheres" is to be understood one in which the rate of corrosion of ordinary mild steel is at least 1 mil. per year, which rate of corrosion is intermediate between those observed at Singapore and at Llanwrtyd Wells (Table IV).

### The Constitution of Alloys of Aluminium with Manganese, Silicon and Iron

(Continued from page 218)

In summarising this latter section the authors state that the range manganese 0-4, silicon 0-4, iron 0-4% has been studied in detail, and a few additional alloys, in the neighbourhood of the ternary eutectic points, have also been investigated. No new quaternary compounds were detected, and all the constituents could be traced back to the component binary or ternary systems.  $\alpha$ (Fe-Si) and  $\alpha$ (Mn-Si) are the end members of a continuous series of solid solutions. Six primary regions occur in alloys containing up to 4% silicon, due to aluminium  $\text{FeAl}_3$ ,  $\text{MnAl}_3$ ,  $\text{MnAl}_6$ ,  $\beta$ (Mn-Si), and  $\alpha$ ; the surfaces separating these fields have been explored, and their intersections traced to the invariant points.

In alloys containing from 7.5 to 12% silicon, the primary aluminium region is bounded by two other binary surfaces, marking the limits of the primary  $\beta$ (Fe-Si) and primary silicon fields.

Aluminium forms binary eutectic surfaces with  $\text{FeAl}_3$ ,  $\text{MnAl}_3$ ,  $\alpha$ ,  $\beta$ (Fe-Si), and silicon;  $\text{FeAl}_3$  forms similar surfaces with  $\text{MnAl}_3$ ,  $\text{MnAl}_6$ , and  $\beta$ (Mn-Si). The remaining binary surfaces involve peritectic reactions. These reactions rarely proceed to completion during solidification; envelopment is of frequent occurrence and causes the persistence of many metastable constituents. Lack of equilibrium is also often caused by undercooling and by the unsaturation of the solid phases.

The quaternary invariant points are four in number:—

Liquid,  $\text{MnAl}_3$ ,  $\text{FeAl}_3$ ,  $\beta$ (Mn-Si),  $\text{MnAl}_6$ , at manganese 3.85, silicon 0.35, iron 2.35%; 731° C.

heading. Comparable tests of different piling procedures have been made at Sheffield and Llanwrtyd Wells over a period of five years. It is concluded from the results that reworking the iron once improves the resistance to atmospheric corrosion. There is no evidence that reworking more than once has any additional effect on the corrosion resistance.

With regard to conditions of exposure, three aspects are discussed—viz., height from the ground; horizontal versus vertical surfaces; and the effect of rust.

#### Protection of Steel by Galvanised Coatings

Two sets of hot-galvanised specimens—i.e., twelve specimens in all—were included in the first series of tests on ordinary and copper-bearing steels X, Y and Z, exposed at Llanwrtyd Wells. In each set, two specimens of each steel were coated, the difference being that in the second set 0.5% of copper was deliberately added to the zinc bath. The average weight of coating was approximately 2.1 oz. of zinc per sq. ft. of surface, corresponding to a calculated thickness of 0.0035 in.

The specimens have now been under observation for eleven years. The only sign of failure so far noticed is the development of isolated rust spots on the coating, not greater in size than a pin-head. These were first recorded towards the end of the fourth year of exposure. These rust spots have shown no tendency to spread or increase in numbers during the last five years, and it is doubtful whether any practical significance should be attached to them, particularly as the total number on the 24 surfaces exposed was only 20 at the last inspection.

Liquid,  $\text{FeAl}_3$ ,  $\beta$ (Mn-Si),  $\text{MnAl}_3$ ,  $\alpha$ , at manganese 2.60, silicon 1.35, iron 2.35%; 695° C.

Liquid,  $\text{FeAl}_3$ ,  $\text{MnAl}_3$ ,  $\alpha$ , aluminium, at manganese 0.35, silicon 1.75, iron 2.00%; 648° C.

Liquid,  $\alpha$ ,  $\beta$ (Fe-Si), aluminium, silicon, at manganese 0.2, silicon 11.7, iron 0.6%; 575° C.

All these involve peritectic reactions. There is no true quaternary eutectic in the aluminium-rich alloys; in all of them final solidification occurs either at the ternary eutectic of aluminium,  $\alpha$ , and silicon, or at the ternary eutectic of aluminium,  $\beta$ (Fe-Si), and silicon, depending upon the composition and also upon the extent to which undercooling and diffusion of iron into the solid phases has occurred during the early stages of solidification.

A brief review is given of the constitution of alloys of aluminium and manganese containing silicon and iron as incidental impurities, and of the effect of varying the amount of these impurities present. In the aluminium-rich alloys, a small quantity of the manganese is taken into solid solution by aluminium or  $\text{FeAl}_3$ , whilst the remainder occurs either as  $\text{MnAl}_6$  or associated with iron and silicon as  $\alpha$ . The silicon is partly dissolved in aluminium, partly combined as  $\alpha$  or  $\beta$ (Fe-Si), and partly present in the free state. Iron occurs as  $\text{FeAl}_3$ , dissolved in  $\text{MnAl}_6$ , or combined as  $\alpha$  or  $\beta$ (Fe-Si). The peritectic reactions involving the formation of  $\alpha$  from  $\text{MnAl}_6$  or  $\text{FeAl}_3$  tend to proceed to completion during hot working or annealing, with consequent reduction in the amount of free silicon.

No attempt has been made to study equilibrium conditions, and the work has been confined to the examination of slowly cooled alloys.

# The Brittle Constituent of the Iron-Chromium System (Sigma Phase)

The existence of this second phase in the binary iron-chromium system has been recognised by many investigators for some years, but its constitution has remained an unsolved problem. In more recent work, which forms part of a larger investigation, the existence of this second phase has been confirmed and its boundaries have been established down to a temperature of 600° C. The presence of cold work has been found to have an accelerating effect on the rate at which the  $\alpha$  constituent can be produced in the alloys.

ONE of the most interesting problems in the field of ferrous metallurgy concerns the occurrence of the sigma phase in high-chromium steels. From a theoretical point of view, interest centres on the constitution of the phase which is still an unsolved problem; the X-ray pattern which it gives is complex, suggesting that its crystal structure is also complex and probably possesses only a low order of symmetry, but it has not yet been found possible to calculate the crystal form which would give rise to the recorded X-ray pattern. From a practical aspect, the ascertained properties of the phase, more particularly its great hardness and extreme brittleness, indicate the desirability of obtaining definite knowledge as to the limits of its existence in order that its production in commercially used alloys may be avoided, or at least minimised.

Investigations carried out in various laboratories during the last 15 years or so have enabled ternary diagrams to be drawn which mark the approximate ranges of composition within which the sigma phase may be produced at various temperatures in iron-chromium alloys containing, in addition, nickel or manganese or silicon. Its production in certain other ternary or more complex alloys of iron and chromium has also been indicated. A summary of existing data on this practically important subject was given in these columns about three years ago.<sup>1</sup> At that time, however, as was pointed out, accurate information was lacking as to the temperature and composition limits within which the phase could form in pure iron-chromium alloys; there was even some doubt as to its existence in such alloys because Adcock,<sup>2</sup> in his detailed investigation of the structure and properties of what were probably the purest iron-chromium alloys ever produced, had failed to find evidence of its existence, and although a good reason for its non-formation, under Adcock's experimental conditions, had been given by Jette and Foote,<sup>3</sup> probably the doubt still remained in some quarters.

These doubts have now been cleared up and the probable phase boundaries indicating the limits of existence of the phase in pure iron-chromium alloys determined as a result of work carried out by A. J. Cook and F. W. Jones at the National Physical Laboratory under the direction of Dr. Sykes, the results being given

in a paper to be presented at the autumn meeting of the Iron and Steel Institute.<sup>4</sup>

In the first place Cook and Jones, who used for their investigations a number of the high-purity alloys actually prepared by Adcock, confirm the opinion expressed by Jette and Foote that Adcock's failure to produce the sigma phase in the very pure alloys he examined was due to the extremely slow rate at which the  $\alpha \rightarrow \sigma$  transformation occurs in such alloys when they are softened and are reasonably free from internal stress; the periods of annealing at 600° C., or thereabouts, which Adcock used were not nearly long enough to effect even a partial change to the sigma form.

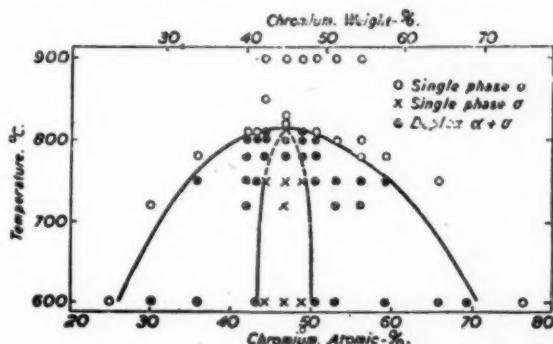


Fig. 1.—Iron-chromium phase diagrams over the range 25-76% chromium.

The authors also found—again in agreement with Jette and Foote—that the rate of the  $\alpha \rightarrow \sigma$  transformation was very greatly accelerated by prior cold work. As an example, they record that filings from an alloy containing 53 atomic per cent. of chromium reached equilibrium as a two-phase ( $\alpha + \sigma$ ) system in two days at 720° C., whereas the bar from which the filings were obtained—which had been vacuum annealed for 12 hours at 1,300° C. by Adcock, and was therefore entirely in the  $\alpha$  condition—had not even started to transform to the sigma phase after 37 days at the same temperature. They also mention that transformation in bar material was markedly accelerated by hammering, and that local effects were produced at sawn surfaces.

The phase boundaries shown in Fig. 1 were determined by X-ray examination of filings from 13 alloys,

<sup>1</sup> "The Brittle Phase in High Chromium Steels," J. H. G. Monypenny, METALLURGIA, March, 1940, p. 143; July, 1940, p. 87.

<sup>2</sup> *J. Inst. I. & S. Inst.*, 1931, ii, 147.  
<sup>3</sup> *Metals and Alloys*, 1936, VII, 267.

<sup>4</sup> "The Brittle Constituent of the Iron-Chromium System (Sigma Phase): I.—A Survey of the Limits of the Sigma Phase in the Binary System,"

covering the range of composition between 26 and 71 atomic per cent. of chromium, the filings being sealed in silica capsules evacuated to a pressure of the order  $10^{-4}$  mm. of mercury before they were subjected to any further heat-treatment. The X-ray patterns of these filings were determined after heating for various times at temperatures between  $600^{\circ}$  and  $900^{\circ}$  C. Preliminary tests on samples containing 40-50 atomic per cent. chromium indicated that stability in structure in this region could be attained at  $600^{\circ}$  C. in five days. Tests on alloys near the limiting compositions at  $600^{\circ}$  C. also indicated that no further change in the relative proportions of the phases occurred in such alloys when the annealing time was prolonged beyond 20 days; it was assumed, therefore, that equilibrium was attained in these various alloys at the end of these periods of annealing.

The structures resulting from annealing at various temperatures between  $600^{\circ}$  and  $900^{\circ}$  C. are shown diagrammatically in Fig. 1. Annealing at  $600^{\circ}$  C. was done for periods up to 60 days, and at this temperature, and up to  $750^{\circ}$  C., the phase boundaries were finally fixed by estimating from the relative intensity of the lines of the phases in the X-ray powder diagrams the amount of the sigma phase present in the duplex alloys; they are considered to have a probable accuracy of about  $\pm 1\%$ .

Treatment at  $820^{\circ}$ , or higher, produced a pure  $\alpha$  structure in all alloys, irrespective of whether the original structure was  $\alpha$ ,  $\sigma$  or a mixture of the two; consequently, it is concluded that the upper limit of the  $\sigma$ -phase boundary is below  $820^{\circ}$  C. At  $820^{\circ}$  C. the  $\sigma \rightarrow \alpha$  transformation was rather sluggish; thus, an alloy containing 46.8 atomic per cent. chromium, and previously treated so as to consist entirely of  $\sigma$ , had a duplex ( $\alpha + \sigma$ ) structure after seven days at  $820^{\circ}$  C., but became pure  $\alpha$  after 24 days. At somewhat higher temperatures, however, the reaction speed increased greatly; thus a pure  $\sigma$  structure was converted to pure  $\alpha$  after 11 days at  $830^{\circ}$  C., whereas 1 hour at  $840^{\circ}$  C. sufficed to bring about a 95% conversion.

At temperatures of  $780^{\circ}$ - $810^{\circ}$  C., however, annealing for about 25 days failed to produce equilibrium in alloys containing 46-50 atomic per cent. chromium. As either the  $\alpha$  or the  $\sigma$  phase—or the two together—could exist in these alloys for such long periods at these temperatures without any noticeable change, the authors concluded that this was a case of true hysteresis and that there was little possibility of establishing accurately the boundary of the pure sigma phase in this temperature interval; hence, in Fig. 1, the broken lines mark what they deem to be the approximate boundaries. The uncertainty does not extend to the outer boundaries of the duplex fields in the same temperature range because alloys containing 36-43% and 50.5-59% did not show any marked hysteresis. As a result of the hysteresis observed in the 46-50% chromium alloys, however, it follows that whatever structure one of these alloys may possess as a result of prior treatment—whether this initial structure be  $\alpha$  or  $\sigma$ , or a mixture of the two—it is unlikely to change if the alloy is heated for long periods of time between  $780^{\circ}$  and  $810^{\circ}$  C. It may be noted in this connection that Jette and Foote<sup>5</sup> considered that the  $\alpha \rightarrow \sigma$  transformation was reversible at a temperature between  $775^{\circ}$  and  $800^{\circ}$  C. They prepared a pure alloy containing 50.6 atomic per cent. iron in both the  $\alpha$  and  $\sigma$  forms,

and found that annealing for 22 hours at  $800^{\circ}$  left the  $\alpha$  form unchanged, but converted the  $\sigma$  into a mixture of  $\alpha + \sigma$ , with the latter predominating. Annealing for 44 hours at  $775^{\circ}$ , on the other hand, left the  $\sigma$  form unchanged, but converted the  $\alpha$  form into a mixture of  $\alpha + \sigma$ . Evidently the transformation in their alloy took place much more readily than in the alloys prepared by Adcock. Possibly this resulted from their alloy having received a greater amount of cold work during its preparation as a powder, though it may be noted that Cook and Jones state that the presence or absence of cold work did not eliminate the hysteresis effects which they describe.

The phase boundaries in Fig. 1 have several interesting features. In the first place, they show that the pure phase is formed at  $600^{\circ}$  C. in alloys containing 44 to 50 atomic per cent. chromium, and not solely at 50%. The authors thus disagree with Bradley and Goldschmidt,<sup>5</sup> who stated the pure phase is formed only when chromium and iron are present in equal atomic proportions, but confirm the results of several of the earlier investigators who found it could occur over a range of composition. Secondly, the curve giving the upper temperature limit of the existence of the phase appears to reach a maximum at about 47 atomic per cent. of chromium; if the views of the earlier German investigators that the phase consists of the compound FeCr are correct, one would expect the maximum to be at 50 atomic per cent. Incidentally, if the phase is essentially this compound, Fig. 1 indicates that it is able to dissolve an appreciable amount of iron but little or no chromium. Further, the range of composition within which the sigma phase may be formed at  $600^{\circ}$  C. (26-71 atomic per cent. chromium, or 24.6-69.4% by weight) is appreciably wider than has been reported by previous investigators, and, in addition, the slope of the curves marking the outer boundaries of the duplex regions suggests that the composition range may be still wider at lower temperatures, though the time required for its formation at these temperatures would probably be very prolonged.

In addition to their X-ray work on filings, the authors also experimented with samples large enough for microscopic examination. The rate of transformation in such pieces was, of course, slower than in filings, though it could be accelerated appreciably if the sample was previously hammered cold. Thus, a sample of a 46.8 atomic per cent. chromium alloy, which had not been subjected to cold work, except that due to sawing the specimen, was converted completely into the sigma phase by annealing for five weeks at  $720^{\circ}$  C. A similar sample of an alloy containing 48.8% chromium was cold-hammered, and then required only 24 days at  $620^{\circ}$  C. (at which the reaction rate, other things being equal, is presumably slower than at  $720^{\circ}$  C.) to produce the same effect. The authors omitted the cold-hammering in a number of their tests, however, as they found that it produced rather confusing strain markings in the alpha phase during subsequent annealing.

The micro-structures which the authors obtained are in line with previously published descriptions of the appearance of the sigma phase. Samples consisting wholly of this phase caused considerable trouble during polishing owing to their friable nature, the polished surfaces showing large fissures and holes. In duplex samples the sigma phase appeared to have developed

first along the original  $\alpha$ -grain boundaries, though separate patches appeared occasionally in the body of the  $\alpha$  grains. Once this nucleus network had formed, however, it seemed that transition to the  $\sigma$  form continued in a random manner in the interior of the grains. The  $\sigma$  phase in such duplex structures was plainly fissured, even when it existed as a relatively thin boundary network. The authors mention that alloys containing the sigma phase did not exhibit the same passivity to etching reagents, which was so marked a feature of the same alloys when they consisted solely of the  $\alpha$  form. The microstructures reproduced in the paper which are excellent samples of metallurgical photomicro-

graphy, were obtained by electrolytic etching in Vilella's reagent, the etching time being of the order of 20 secs.

The title of the paper indicates that it records only the results of part of a larger investigation which, it may be noted, is being sponsored by the Alloy Steels Research Committee. In view of the interest and importance of the subject, both from theoretical and practical aspects, it is to be hoped that the publication of this excellent piece of research will be followed, without undue delay, by that of further work, in which the formation of the sigma phase in ternary and still more complex alloys of iron and chromium will be examined with the same care and thoroughness.

## The Maintenance of the Furnace Linings in Large Basic Open-Hearth Tilting Furnaces\*

By A. Jackson

(Appleby-Frodingham Steel Co., Ltd.)

APPLEBY-FRODINGHAM steel furnaces have always used more chrome ore and magnesite paste for lining repairs than chrome-magnesite and magnesite as bricks. Before 1939 the materials used for making this paste were relatively cheap, and their use was therefore economic.

Since 1939 considerable efforts have been made, first to reduce the magnesite consumption, even at the expense of increasing the chrome ore, later to reduce the chrome ore as well as magnesite consumed, and finally to replace both of these materials to the greatest possible extent by substitutes.

TABLE I.  
ANNUAL CONSUMPTION OF CHROME ORE, MAGNESITE AND SERPENTINE.

Period.	Consumption, Lb. per Ton of Ingots, of—	Magnesite,	Serpentine,
	Chrome Ore, etc.		
1936-1939	5.90	6.25	Nil
Year ending June, 1940	10.45	5.28	Nil
1941	8.80	4.58	Nil
1942	7.04	4.06	Nil
1943	2.09	2.84	3.45

Table I shows the annual consumption of chrome ore, magnesite and serpentine per ton of production over the last four years, compared with pre-war averages for the 250- and 300-ton furnaces at the Appleby plant.

The figures for "magnesite, etc., " consist of magnesite and chrome-magnesite brick end recoveries (comprising some 50% of all bricks used) and double-burned magnesite peas. Only a small proportion of the above materials is used on portions of the furnace other than the front lining.

The points affecting the changes in consumption are as follows:—

(1) The percentage of chrome ore in the paste was increased considerably, and some magnesite saving resulted.

(2) The chrome ore percentage was steadily reduced to give a minimum total consumption of chrome ore plus magnesite.

(3) The front bank was fettled after the whole of the scrap, etc., was charged, but before the addition of the hot metal. This enabled pasting to commence at a slightly higher level, but used more dolomite.

(4) Stable dolomite cement was used in place of magnesite powder for rebuilds.

(5) Water-cooling of the front lining was used earlier, but was abandoned near the end of 1942.

(6) More basic bricks were used in the splays, and less patching paste therefore necessary.

These points were responsible for the alteration up to about the end of 1942.

Concerning the use of serpentine, laboratory trials, commenced in June, 1942, showed that an 80/20 mixture of serpentine-magnesite (the magnesite being largely in the fine fraction) best satisfied the combined requirements of refractories and economy of chrome ore and magnesite. Subsequent practical trials confirmed this view. Mixtures of chrome ore and serpentine were definitely less good and were considered unsatisfactory for this purpose.

This new paste was again a stage less good than the material that it replaced. In consequence, as the front of the furnace was continuous steel plate, shut-downs for repairs became more frequent.

To overcome this trouble the structural work of the furnace front was strengthened and openings were cut through the plate-work between each door, which could be covered during operations by a detachable steel plate wedged into position. By this means some new brick-work could be put into the lining without taking the furnace off. It was only with reluctance that the continuous steel-cased front was abandoned, but only the possibility of putting in new brickwork by this means, coupled with the fact that the doors on Appleby furnaces are relatively close together and have narrow jambs, easily accessible for pasting, enabled this serpentine material to be used. Some extra chrome-magnesite brick is now used, but much less than the saving in chrome ore and magnesite resulting from the alterations.

The older tilting furnaces of smaller capacity at the Frodingham melting shop have only three doors, and consequently very wide jambs. Furthermore, the design of the furnace front will not permit of alteration on the above lines; we have, therefore, not as yet been able to adapt, with any degree of satisfaction, the less good type of paste to this plant.

The following is the grading of the 80/20 serpentine-magnesite paste:—

Moisture content, 22.8%.  
Grading on British Standard sieves:—

	%
On 7 mesh	1.0
" 7-25 mesh	27.0
" 25-72 mesh	29.0
" 72-150 mesh	12.5
Through 150 mesh	30.5
	100.0

\* Iron and Steel Inst., August, 1943. (Advance copy.)

# The Structural Changes Effected in 70:33 Brass Strip by Cold Rolling and Annealing

By Maurice Cook, D.Sc., Ph.D., and T. LI. Richards, B.Sc., Ph.D.

*The effect of progressively increasing cold-rolling reductions, and of subsequent annealing on the structure and properties of 70 : 33 brass strips, of three different initial grain sizes, has been studied by X-ray and microscopic methods. The work is reported by the authors in the JOURNAL OF THE INSTITUTE OF METALS,\* from which this account has been abstracted.*

MANY investigators<sup>1-10</sup> have studied the problem of directionality in rolled and annealed brass strip, but the nature of the mechanisms of deformation on cold rolling and recrystallisation on subsequent annealing are not yet fully understood. The purpose of the work described by the authors in the present paper was to obtain more information concerning the structural changes which take place in these operations, and to correlate these changes with the mechanical properties and cupping characteristics of the strip.

Three series of strips, each with random orientation of crystals, but with different grain sizes, were rolled with reductions in thickness ranging from 10 to 95%, and subsequently annealed at temperatures ranging from 400° to 800° C. This material was examined both in the cold-rolled and annealed conditions by X-ray and microscopic methods. The hardness of the strips was determined, and cupping tests were carried out on annealed material. The mechanical properties of selected strips in various directions were determined, and annealing curves were established for strips of the three series rolled with reductions of thicknesses of 40, 70 and 95%.

The metal used in the investigation was all obtained from one 1,000-lb. ingot of phosphorus-free brass of the following composition—copper, 69.25%; tin, 0.01%; lead, 0.004%; iron, 0.015%; nickel, 0.013%; arsenic, 0.003%; zinc (by difference), 30.71%. The ingot, which measured 3ft. × 2 ft. × 3½ in., was hot rolled to a thickness of 1½ in. By means of a specified rolling scheme three series were prepared, each of 10 strips, with a random orientation of crystals and the same final thickness of 0.025 in., which had been given progressively increasing rolling reductions in thickness ranging from 10 to 95%. By suitably adjusting the last two process-annealing temperatures, the grain sizes of the strips of the three series prior to the final rolling reduction were made 0.01–0.015 mm. (A), 0.025 mm. (B), and 0.065

mm. (C), respectively. These annealing temperatures were 400° C. for series A, 500° C. for series B, and 575° C. for series C. After the final rolling, the strips were annealed for 1 hour at temperatures of 400°, 500°, 575°, 700° and 800° C.

The samples were numbered according to the key given in the accompanying table:—

KEY TO LETTERING AND NUMBERING OF SAMPLES.

A	Initial grain size	.....	0.01–0.015 mm.
B	"	.....	0.025 mm.
C	"	.....	0.065–0.065 mm.
1	Nominal cold rolling reduction of	.....	10%
2	"	"	20%
3	"	"	30%
4	"	"	40%
5	"	"	50%
6	"	"	60%
7	"	"	70%
8	"	"	80%
9	"	"	90%
10	"	"	95%
1	Final annealing temperature of	.....	400° C.
2	"	"	500° C.
3	"	"	575° C.
4	"	"	700° C.
5	"	"	800° C.

Thus, strip A 9.3 was a strip of a grain size of 0.01–0.015 mm., cold rolled 90%, and finally annealed at 575° C., while strips marked with a letter and one number only were in the cold-rolled condition.

The same technique as that employed by the authors in earlier investigations on copper strip<sup>11,12</sup> was used for the examination of the cold-rolled strip. The results of X-ray examination showed that the degree and type of preferred orientation developed in brass strip by cold rolling was independent of the initial grain size, and was determined only by the magnitude of the final rolling reduction. A pole figure representing the complete distribution of the octahedral planes of the crystal lattice was determined for the strip A 10, and is reproduced in Fig. 1. This figure is in close agreement with that already established by Brick.<sup>7</sup>

The changes in microstructure brought about by cold rolling were studied on etched sections cut parallel to the strip surface, and also on sections in the rolling direction perpendicular to the strip surface. The progressive change in structure with increasing cold-rolling reductions was identical in the three sizes, but the

\* August, 1943, pp. 351–371.

- 1 W. B. Price and P. Davidson, *Trans. Amer. Inst. Metals*, 1916, **10**, 133.
- 2 A. Bass and R. Glocker, *Z. Metallkunde*, 1928, **20**, 181.
- 3 O. Bauer, F. Goler and G. Sachs, *ibid.*, 1928, **20**, 242.
- 4 A. Phillips and C. H. Samuels, *Trans. Amer. Inst. Min. Met. Eng.*, 1937, **106**, 171.
- 5 C. H. Samuels, *J. Inst. Metals*, 1934, **55**, 209.
- 6 M. Cook, *ibid.*, 1937, **60**, 139.
- 7 R. M. Brick, *Trans. Amer. Inst. Min. Met. Eng.*, 1940, **137**, 193.
- 8 R. M. Brick and M. A. Williamson, *ibid.*, 1941, **143**, 84.
- 9 H. L. Burghoff and E. C. Bohlen, *ibid.*, 1942, **147**, 144.
- 10 E. W. Palmer and C. S. Smith, *ibid.*, 1942, **147**, 164.

11 M. Cook and T. LI. Richards, *J. Inst. Metals*, 1940, **66**, 1.

12 M. Cook and T. LI. Richards, *ibid.*, 1941, **67**, 203.

changes were more readily observed in the C strips because of their larger grain size.

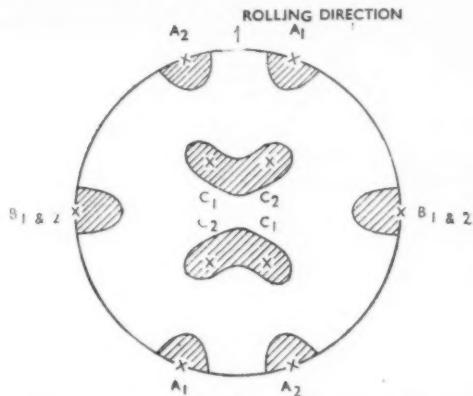


Fig. 1.—A pole figure representing the distribution of the octahedral planes of the crystal lattice (as rolled).

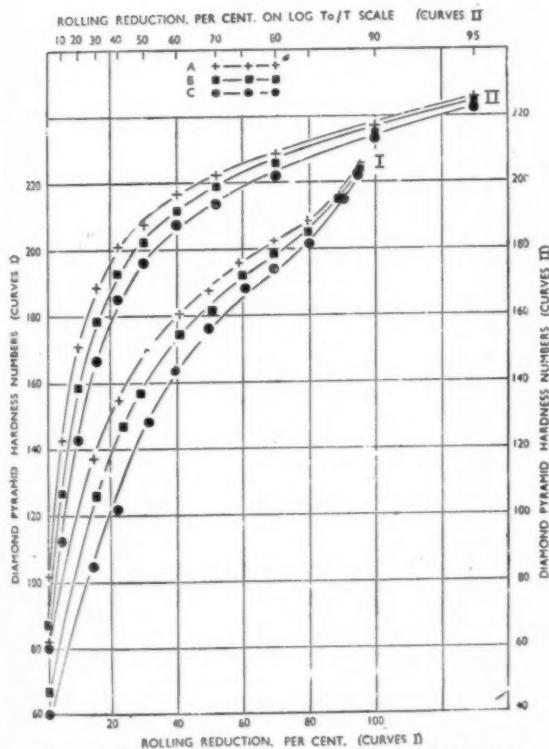


Fig. 2.—Diamond-hardness values of cold-rolled strips.

The evidence of X-ray and microscopic examination makes it clear that the deformation of 70:30 brass during progressively increasing cold-rolling reductions takes place by two mechanisms similar to those already described for copper.<sup>11</sup> Whilst with copper the crystals retain their individuality even after heavy rolling reductions—that is, about 90%, or more, there is evidence that with brass strip rolled in excess of 80% the crystals disintegrate into minute fragments.

The D.P. hardness of the cold-rolled strips was determined, and in Fig. 2 the work-hardening curves, plotted on two scales, are reproduced. In curve I the hardness is plotted in the usual manner against the percentage rolling reduction in thickness, whilst in curves II the hardness is plotted against the degree of deformation, measured by the logarithm of the initial thickness  $T_0$  of the strip divided by its thickness  $T$  after rolling. The work-hardening curves for strips of the three series, A, B and C, have the same form, but the initial difference in hardness is not maintained over the whole range of deformation considered, but decreases appreciably with the heaviest reductions.

Tensile tests were made on samples cut in various directions from strips of the A, B and C series which had been rolled with reductions in thickness of 70 and 95%. The elongation values were very small, and no significant variations in them could be observed. In Fig. 3 the tensile strengths of A 7, B 7, C 7, A 10, B 10 and C 10 strips have been plotted against the direction of test-piece. It can be seen from these curves that initial grain size has no appreciable effect on their form. In all cases the values for tensile strengths are lowest in the rolling direction, and reach a maximum at 90° to the direction of rolling.

The marked directionality observed in such strip might be explained by the presence of the block structure, since during tensile tests carried out on samples cut in the rolling direction, the deformation can proceed by continued crystal break-up and by block gliding on prism faces; whilst in tests on samples cut transverse to the rolling direction the deformation can proceed only by further break-up of the fragments upon new layers transverse to the direction of testing. From such considerations the tensile strength of heavily rolled brass strip would be expected to show a minimum value in the rolling direction and a maximum value in the transverse direction, and also the difference in value in the two directions would increase with increasing degree of deformation.

#### Annealed Material

Systematic X-ray examination was confined to strips finally annealed at 400°C., since this material had a small grain size, and the presence of preferred orientation of crystals in such strip can be detected and analysed more easily than it can in strip of larger grain size.

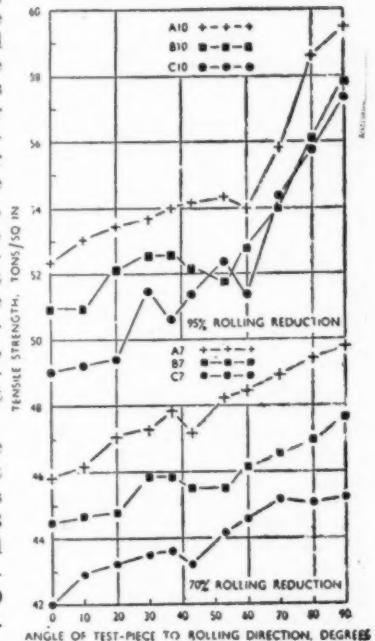


Fig. 3.—Tensile strengths of strips.

obtained by annealing at higher temperatures. Patterns obtained with strips annealed at 400°C. showed that they were fully recrystallised. Both normal transmission photographs and glancing photographs of the annealed strips were taken with the X-ray beam at right angles to the rolling direction.

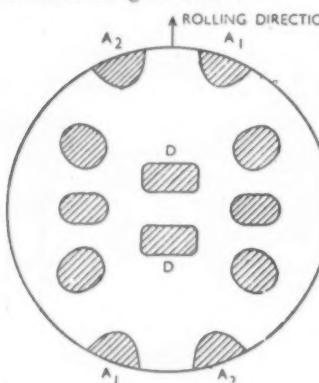


Fig. 4.—A pole figure representing the distribution of the octahedral planes of the crystal lattice (annealed).

structure in a later section dealing with microstructure.

Marked preferred orientation was only observed in the strips of the three series rolled with the two heaviest reductions in thickness—namely, 90 and 95%. The texture ultimately developed by heavy rolling and subsequent annealing was identical in the strips of the three series, and in order to obtain a complete representation of the texture a pole figure showing the distribution of the octahedral planes of the crystal lattice was determined (Fig. 4). This pole figure is in complete agreement with that established by Brick<sup>7</sup> for 70 : 30 brass strip cold rolled 99% and annealed for half an hour at 400°C. By comparing the pole figure of heavily rolled strip, Fig. 1, with that of the same strip subsequently annealed, Fig. 4, it can be seen that a definite reorientation of the structure has taken place on annealing.

It has been shown<sup>2</sup> that this annealed texture can be represented by preferred orientations in which the crystals are aligned with a {113} plane parallel to the strip surface and a <112> axis in the rolling direction, but no satisfactory explanation has yet been given of how this texture arises from the original rolled texture.

Samples of strip rolled with different reductions, and subsequently annealed at 400°, 500°, 575°, 700° and 800°C., were examined microscopically on sections parallel to the surface and on sections in the rolling direction perpendicular to the strip surface. In all series, i.e., irrespective of the grain size before final rolling, the grain size of strips annealed finally at 400°C. decreases with increasing rolling reduction, but with higher annealing temperatures the effect of variation in the magnitude of the final rolling reduction is not very marked at any one temperature. The degree of uniformity of grain size in the finally annealed strip is, however, affected by the initial grain size and by the rolling and annealing conditions, particularly when the final rolling is limited to reductions up to about 40%.

With increasing final annealing temperature there is the usual increase in grain size, but in none of the strips

examined was there any instance of abnormal crystal growth such as has been shown to occur in copper under certain conditions.<sup>13</sup> The annealed brass strip exhibited no characteristic etching features which could be associated with the preferred orientation of the crystals such as were observed in copper strip,<sup>12</sup> and it was not

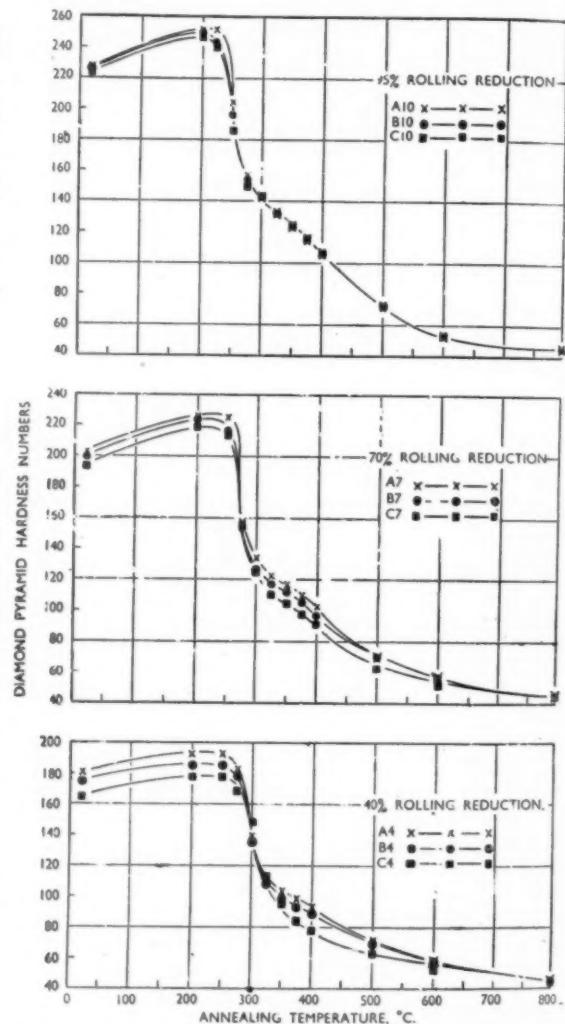


Fig. 5.—Annealing curves based on diamond-hardness determinations.

possible to distinguish between the various samples except by the closest scrutiny of the directions of twining.

Annealing curves based on D.P. hardness determinations on samples of the A, B and C series, rolled with reductions in thickness of 40, 70 and 95%, and annealed for half-hour periods at temperatures ranging from 200° to 800°C., are reproduced in Fig. 5. From these it can be seen that all samples harden appreciably before softening commences.

The amount of this hardening is independent of the initial grain size, but it increases with the magnitude of

<sup>13</sup> M. Cook and C. Macquarie, *Trans. Amer. Inst. Min. Eng.*, 1939, 133, 142.

<sup>14</sup> M. Cook and T. Li. Richards, *J. Inst. Metals*, 1943, 68, 201.

the rolling reduction. The results show the usual lowering of the softening temperatures with increasing amounts of rolling, but in contrast with the observations upon rolled and annealed copper strip,<sup>12</sup> the initial grain size of the brass strip has no influence on the softening temperature.

The results of tensile tests in various directions on samples of the A, B and C series rolled with reductions in thickness of 70 and 95%, and annealed at 575° C., are plotted in Figs. 6 and 7, and it will be seen that difference in initial grain size is without apparent effect either on tensile strength values or on the position relative to the rolling directions at which maximum and minimum values occur.

### Cupping Characteristics

Information on directionality in annealed strips was also obtained by investigating the cupping characteristics of strips annealed at 500°, 575° and 700° C. The cups had an external diameter of 0.510 in., and a height of 0.410 in., and the results of the observations made are recorded in the accompanying table:—

CUPPING TESTS. DIRECTION AND HEIGHT (IN INCHES) OF EARS.

Nominal Cold-rolling Reduction, %.	Series A.			Series B.			Series C.		
	Final Annealing Temperature, °C.			Final Annealing Temperature, °C.			Final Annealing Temperature, °C.		
	(2) 50	(3) 575	(4) 700	(2) 50	(3) 575	(4) 700	(2) 500	(3) 575	(4) 700
(1) 10	45° 0.012	45° 0.020	45° 0.035	45° 0.005	45° 0.008	45° 0.020	Flat	Flat	Flat
(2) 20	45° 0.010	45° 0.018	45° 0.033	45° 0.005	45° 0.004	45° 0.017	Flat	Flat	Flat
(3) 30	45° 0.009	4° 0.015	45° 0.030	Flat	45° 0.005	45° 0.017	Flat	Flat	Flat
(4) 40	45° 0.008	45° 0.016	45° 0.035	Flat	45° 0.006	45° 0.021	Flat	Flat	Flat
(5) 50	45° 0.010	45° 0.018	45° 0.037	Flat	45° 0.008	45° 0.021	Flat	Flat	Flat
(6) 60	45° 0.013	45° 0.022	45° 0.041	45° 0.005	45° 0.010	45° 0.023	Flat	45° 0.005	45° 0.005
(7) 70	45° 0.015	45° 0.024	45° 0.041	45° 0.007	45° 0.015	45° 0.025	Flat	45° 0.010	45° 0.019
(8) 80	45° 0.016	45° 0.022	45° 0.035	Flat	45° 0.013	45° 0.025	Flat	45° 0.007	45° 0.020
(9) 90	55° 0.018	55° 0.024	55° 0.035	55° 0.008	55° 0.010	55° 0.025	60° 0.015	60° 0.015	60° 0.023
(10) 95	55° 0.020	55° 0.028	55° 0.048	55° 0.017	55° 0.025	55° 0.042	60° 0.200	60° 0.24	60° 0.033

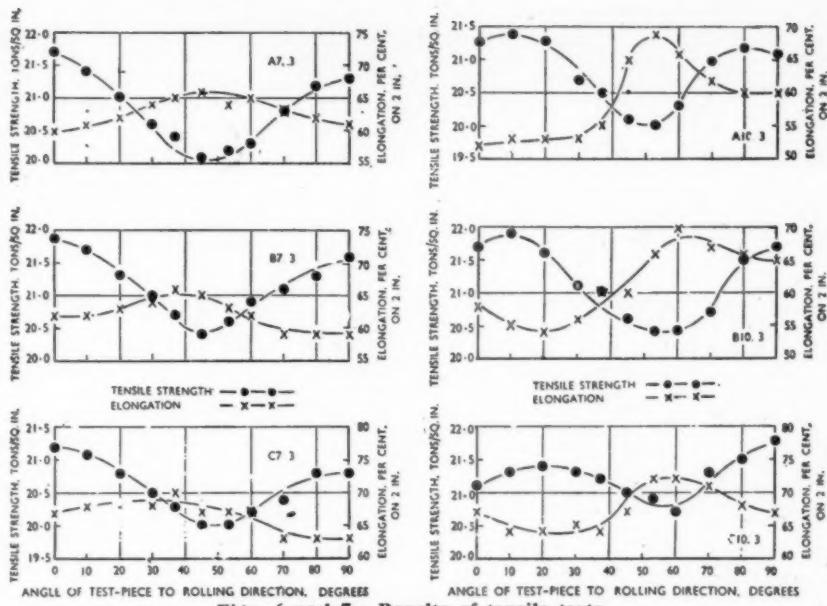
Flat: Flat-topped cups.

45°: Four ears at 45° to the rolling direction.

55°: Four ears at 55° and 125° to the rolling direction.

60°: Six ears at 0°, 60° and 120° to the rolling direction.

\* The 0° ears on these cups were very low and the measurements given are the heights of the ears situated at 60° and 120° to the rolling direction. The cups closely resemble the cups of the A and B series with ears at 55° and 125°.



Figs. 6 and 7.—Results of tensile tests.

In all three series there was a change in the position of the earing as the final rolling reductions increased from about 80 to 90%, which coincided with the change in the type of recrystallisation, the direction of earing again corresponding to the direction in the strip in which the tensile strength was at a minimum (Fig. 7). In the A and B series the type of earing changed from four ears at 45° to four ears at 55° and 125° to the rolling direction. In the cups obtained from the C 10 strips the 0° ears were very small, whilst the 60° and 125° ears were more developed, and these cups closely resembled those cut from corresponding strips of the A and B series having ears at 55° and 125° to the rolling direction. The extent of earing on cups from strip rolled with any given reduction increased with the magnitude of final annealing temperature, except for the flat-topped cups from strips of the C series rolled with reductions up to 50%, which showed no preferred orientation.

### The Nickel-Molybdenum System

NICKEL-MOLYBDENUM alloys were prepared from hydrogen-reduced powders and studied by Ellinger\* both metallographically and by X-rays. The constitutional diagram shows: (1) A eutectic at 2,410° F. and 46.5% molybdenum; (2) a peritectic reaction between liquid and molybdenum-rich solid solution at 2,500° F. to form nickel-molybdenum containing 62% molybdenum; (3) the molybdenum-rich solid solution dissolves 0.9% nickel at the peritectic temperature; (4) the solubility of molybdenum in the nickel-rich solid solution decreases from 37% at 2,410° F. to 30% at 1,635° F., and to 20.5% at 1,110° F.; (5) nickel-molybdenum and the nickel-rich solid solution form  $Ni_3Mo$  at 1,635° F.; (6)  $Ni_3Mo$  and the nickel-rich solid solution form  $Ni_4Mo$  at 1,545° F. The alloys containing 21-35% molybdenum are age-hardenable either by proportion of  $Ni_4Mo$  or  $Ni_3Mo$  and  $Ni_3Mo$ .

\* Ellinger, H., *Trans. Am. Soc. Metals*, 1942, **30**, 607-637.

# Fourth Report of the Oxygen Sub-Committee of the Committee on the Heterogeneity of Steel Ingots\*

*War conditions have interfered with the smooth and regular prosecution of the various researches of this Sub-Committee, and, in consequence, some aspects of the work outlined in previous reports have not yet reached an appreciable state of finality. However, several additional problems have been investigated. Attention has been directed to the determination of gaseous elements other than oxygen, i.e., hydrogen and nitrogen, as they occur in solid materials. The fundamental aspects of the residue methods and their application to a series of alloy steels have received further examination, and the determination of the gas content of liquid steel has been investigated. This report is comprehensive, and it is only possible here to present a summary of the conclusions of the individual contributions.*

**D**ESPITE difficulties resulting from the continuance of the war the Oxygen Sub-Committee<sup>1</sup> has carried out a considerable amount of work on the determination of gaseous elements, as they occur in solid materials, and also the gas content in liquid steel, since the publication of the last report.<sup>2</sup> Various methods applied have received further examination. The vacuum fusion method continues to be applied to specialised problems, such as the surface films on metals.

In view of the more or less stabilised nature of the methods of examination, and their extension to deal with other gases, it has been thought desirable to modify the scheme of the Sub-Committee's Reports. Section II, which is sub-divided into parts under the main headings of oxygen, hydrogen and nitrogen, deals with improvements and modifications introduced into the methods of determination of each of these elements. Section III deals with the application of these methods to several specialised problems, viz., surface films on metals, rimming steels, ferro-alloys, acid and basic slags, and to a series of alloy steels, including high silicon-iron. Certain of these contributions are of an individual character, but much work in others has been of a collaborative character, and the results of the Sub-Committee's co-operative examination are given in the section on the alloy steels, which is a continuation of an alloy steel series examined in a previous report.<sup>3</sup>

## SECTION II—METHODS OF ANALYSIS.

### Part A.—Determination of Oxygen

**The Vacuum Fusion Method.**—This method, which still remains the accepted standard method for the determination of total oxygen in iron and steel, is discussed by Mr. Sloman. Sources of error which have been observed during investigations on alloy steels and ferro-alloys are mentioned, and are associated particularly with the presence of volatile metallic constituents.

Mr. Sloman's contribution also contains an account of a series of experiments on a 13% manganese steel, undertaken to study the effect of the manganese-film formation on the oxygen value.

As a result of the work which has been carried out since the last report, it has been confirmed that, provided suitable precautions are taken where necessary, the method gives accurate results for oxygen, hydrogen and nitrogen on all classes of ferrous materials. As regards oxygen, alumina is the only oxide which is sufficiently stable to present difficulties, and the examination of alloy steels containing aluminium has shown that even this oxide is quite rapidly reduced at about 1,600° C. In no case has the evolution of hydrogen been found to be either incomplete or sluggish, even at temperatures as low as 1,550° C. One or two nitrides which are not completely reduced at 1,550° C. have been noted. They occur in steels containing chromium and titanium, but no difficulty is experienced if the reaction is allowed to proceed at 1,600° C., or over.

**The Fractional Vacuum Fusion Method.**—Further experience with the fractional modification of the vacuum method is described by Dr. Swinden, Mr. Stevenson and Mr. Speight. One of the main difficulties of this method lies in the separation of iron and manganese oxides which, even with pure and separate oxides, is incomplete owing to the small temperature interval between the melting point of the iron-carbon-tin alloy and the temperature at which manganese oxide is readily reduced. Attempts have been made to increase this interval by reducing the melting point and, consequently, the reduction temperature of the iron oxide, with the object of obtaining sharper separation of iron and manganese oxides. Additions of copper and silver have been made, with but only slight reduction of the melting point, and increased practical difficulties, such as an increased "blank," volatility of the alloy metal and reduced carbon solubility, have rendered such modifications of doubtful value.

The position remains that no indication of the validity of the fractional method, other than comparison with known residue extraction methods, is as yet available. As indicated by earlier work, it is known that

\* Paper No. 22/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Oxygen Sub-Committee and published by the Iron and Steel Institute as an Advance Copy, July, 1943, 192 pp.).

<sup>1</sup> A Joint Committee of the Iron and Steel Institute and The British Iron and Steel Federation, reporting to the Iron and Steel Industrial Research Council.

<sup>2</sup> Third Report of the Oxygen Sub-Committee, *Jour. I.S. Inst.*, 1941, No. 1, pp. 295P—387P.

<sup>3</sup> Second Report of the Oxygen Sub-Committee, Iron and Steel Institute, 1939, Special Report No. 25, 216 pp.

with inclusions of simple type, e.g., single oxides, separation is reasonably accurate, although this may not hold for more complex compounds.

Further experience of the fractional method has confirmed previous findings regarding the significance of fractional results on normal killed steels. In comparison with residue methods, there is a tendency for: (a) The iron-oxide to be lower, (b) the manganese-oxide fractions to be higher, and (c) silica and alumina results to be lower. The results of an interesting application of this method to a study of weld-metal deposits are included.

*The Aluminium Reduction Method.*—This relatively inexpensive and rapid method is operated either in hydrogen atmosphere or under reduced pressure, and has given results in very close agreement with those of vacuum fusion, and, according to Mr. Gray and Mr. Sanders, it continues to be used with success. Two modifications have been introduced at the Central Research Department of the United Steel Companies, Ltd. :—

(1) The furnace tube and rubber bung have been replaced by a silica tube and ground joint, the ground joint being connected to a Pyrex adaptor and stopcock. This is to minimise the possible air leak to the evacuated tube when using the older apparatus.

(2) A modified graphite boat, incorporating a detachable lid, is now used. The purpose is to reduce possible error due to small pieces of silica being flaked from the tube and falling into the aluminium-alloy metal, thereby reacting to form alumina.

*The Chlorine Method.*—In this sub-section Mr. Colbeck and Mr. Craven describe experiments on the effect of increased chlorination temperatures on the composition of the residue obtained in the normal chlorination at 350° C. Increased chlorination temperature is necessitated by the presence in steel of alloying elements, particularly large amounts of chromium. The work on the increased chlorination temperature has been confined to the examination of one sample of steel, therefore no definite conclusions can be drawn from the results given, but the figures do give a general indication of the behaviour of the various oxides when the basic oxides are combined with silica and alumina, and are not present simply as FeO or MnO. Both the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  fractions remain substantially unaffected by an increase in temperature up to at least 550° C. A small decrease, as shown in the recovery of the two oxides at 700° C., may be significant of the commencement of attack. At 450° C. the recovery of FeO is slightly less than at 350° C., while at 550° C. the amount of this oxide remaining in the residue represents only about 50% of that retained at 350° C. The amounts of MnO found in the residues appear to be fairly constant up to 500° C. but at 700° C. the rate of attack is very rapid.

These broad conclusions drawn from the results of the experiments are consistent with the findings of Wasmuht,<sup>4</sup> who approached the problem from a different angle.

*The Alcoholic Iodine Method.*—The fundamentals of this method have received further attention, and in this sub-section a critical summary of three papers dealing with various aspects of the method is presented. In one paper Mr. Rooney describes experiments on the

effect of the water content of the methanol solvent, and shows that the presence of water causes an increase in the content of iron oxide found in the separated residue. Control of the purity of the methanol supplies as received by using sensitive hydrometers is suggested by Mr. Rooney as a means of avoiding unnecessary purification of the methanol by distillation over calcium. In another paper Mr. Speight discusses the behaviour of carbon and phosphorus in the alcoholic-iodine method, and their effect on the composition of the separated residue. A suggested explanation based on adsorption is put forward in connection with the contamination of the residue by oxides of these two elements. The possibility of a similar effect in the case of other constituents of the residue is also indicated, and the need for subsequent treatment of the residue to remove the excess contamination is stressed. Initial experiments using a solution of ammonium tartrate for this purpose have given a qualified success. As indicated in the Third Report of the Oxygen Sub-Committee, it is not unusual for an accepted method to be modified to suit different types of material. Consequently, it must be recognised that decomposition of steel by alcoholic iodine does not necessarily separate only the oxygen-bearing non-metallic inclusions. For a correct measure of the oxygen content, any contaminants present should be identified and their effect on the determination assessed. A similar conclusion is reached by Mr. Rooney, who, in a further paper, of this sub-section, describes the interference due to the presence of aluminium in steel. From three steels containing rather more aluminium than is normally present in carbon steels, alcoholic-iodine residues with excessive contents of alumina were obtained. The alumina was separated by an after-treatment into an insoluble fraction, which presumably occurs as alumina in the steel, and a soluble portion, comprising other aluminium compounds separated during the alcoholic-iodine extraction. By these experiments our knowledge of the limitations and uses of the alcoholic iodine method has been definitely advanced. It can be stated, therefore, that the range and usefulness of this method have been extended, and some of the limitations listed in the previous report have been removed.

*The Aqueous Iodine Method.*—This method, on which Mr. Westwood reports progress with its application to pig and cast iron, continues to be used substantially as described in the Third Report of this Sub-Committee. Several of the samples previously reported have been re-examined and revised figures are included. Examination of the results of this investigation shows such small variations between the amounts of individual oxides in different samples, and such small total-oxygen content, that attention is now being directed to methods yielding a total oxygen figure, aluminium reduction and vacuum fusion, which are likely to be adequate for present purposes.

In order to bring the aqueous-iodine method into line with other methods, and to avoid the difficulty of surface oxidation, several attempts have been made to use solid specimens instead of drillings. It was found possible to dissolve the sample completely by prolonging the time of stirring, but there is not yet sufficient evidence to enable any conclusion to be drawn with regard to replacing drillings by solid specimens in the recommended procedure. A little work has also been done on samples

<sup>4</sup> *Zeitschrift für angewandte Chemie*, 1930, 43, pp. 98-101, 125-129.

<sup>5</sup> Eighth Report on the Heterogeneity of Steel Ingots, p. 43, *The Iron and Steel Institute*, 1939, Special Report No. 25.

taken from various parts of the pig, but any evidence of heterogeneity due to this cause is not yet sufficient for issue.

### Summary

The position, therefore, with regards to methods of analysis for oxygen in iron and steel may be summarised as follows :-

In the vacuum-fusion method we have a thoroughly reliable method of determining the total oxygen in steel and steelmaking alloys. A suitable technique must be employed when the sample has a high content of certain volatile constituents, such as manganese, but the necessary precautions are well established.

The aluminium-reduction method has been extensively examined on a variety of commercial steels, and again, with suitable control, has been found to be uniformly satisfactory for the determination of total oxygen.

It will, however, be readily understood that the determination of total oxygen provides information of only limited value, and, therefore, other methods have been investigated to assess the content of the respective oxides.

The alcoholic-iodine method has been most exhaustively studied and its value and limitations are now reasonably well understood. By this method results comparable with those obtained by the vacuum-fusion process can readily be obtained on plain carbon and low-alloy steels, which, after all, constitute a very large proportion of our steel production. Favourable results have been obtained on some commercial nickel-chromium alloy steels, but stable carbides are a source of interference with the method. Low-carbon rimming steels containing a high proportion of ferrous and manganese oxides do not always furnish satisfactory results.

The chlorine-extraction method gives promise of more successful application to a wider variety of steels, particularly those containing carbide-forming elements, e.g., chromium, but there appear to be limitations to the method, such as are demonstrated in the low results obtained for rimming steel.

The modification of the vacuum-fusion process whereby the extraction is carried out in fractional stages has been shown to produce results in good agreement with those of the orthodox vacuum-fusion method as regards total oxygen, and some interesting results are obtained by this method in separating the oxygen into its constituent oxides. Further work still requires to be done, however, before the process can be claimed to have been established as universally reliable for all combinations of oxides.

Finally, the aqueous-iodine method has been used, with interesting results, by the British Cast-Iron Research Association on pig iron, although the Sub-Committee prefer to express no opinion as to its reliability when dealing with steel samples.

### Part B.—Determination of Hydrogen

Methods for the determination of hydrogen in steel are discussed by Dr. Newell. Almost all these methods involve vacuum extraction of the hydrogen at high temperatures, either above or below the melting point of the alloy. Hence, not only is hydrogen determined by the vacuum-fusion process, but also by the vacuum-heating method at temperatures of the order of 600° C. The Sub-Committee, as a whole, are satisfied that melting *in vacuo*, under the conditions advocated for oxygen

determinations, does liberate all the hydrogen present in steel. The vacuum-fusion apparatus, however, suffers the disadvantage that very high temperatures, of up to 2,000° C., or more, are required for the initial degassing operation, and the technique necessary for dealing with such apparatus, as well as the apparatus itself, is quite elaborate.

Much work has been done on vacuum extraction, and Sloman,<sup>5</sup> who is responsible for much pioneer vacuum-extraction work done in Britain, showed that at 650° C. the evolution of hydrogen normally ceased after 1-2 hours, and that the amount so collected was equal to that collected by vacuum fusion at 1,550° C. Dr. Newell examined the rate of hydrogen evolution from steel over the temperature range of over 400° to 900° C.,<sup>6</sup> and showed that normally an hour at 600° C. was sufficient for the complete evolution of the hydrogen free from all but traces of other gases, and gave results indicating that for a range of alloy steels vacuum heating at 600° C. was as satisfactory for hydrogen determination as vacuum fusion at 1,600° C. For this purpose a simple type of glass apparatus was designed and constructed, in which steel samples could be manipulated in and out of a clear-silica-tube furnace by the novel principle of a "mercury life," by means of which contact between the steel and the furnace wall and any possible interaction were avoided. The advantages of operating under these conditions, as compared with those for vacuum fusion, are that the estimation of the hydrogen is made simply by measurement of its pressure at a definite volume and that the blank is negligible, amounting to only 0.00001 ml. (or 0.000,000,001 g.) per hour, which is only one-hundredth of the corresponding blank obtained under optimum conditions by the vacuum-fusion method.

Since the publication of the paper just referred to, a number of laboratories have installed somewhat similar equipment and for the same purpose. In the following sub-section the author deals with further developments in the apparatus at the Brown-Firth Research Laboratories, whilst in the subsequent two sub-sections accounts are given of experience gained with equipment set up in the Central Research Department of the United Steel Companies, Ltd., and in the Research Department of I.C.I. (Alkali), Ltd. All three laboratories agree as to the value of the method in the investigation of the hydrogen content of steel, and the publication of this report brings forward extended evidence of its utility and reliability.

One of the difficulties that one encounters when trying to compare the merits of different methods of determining hydrogen in steel is that there is no certainty that two specimens from the same sample do really contain the same amount of hydrogen. When sectioning ingots the author has found as much as a five-fold variation of hydrogen content between the centre and outside of the ingot, maybe over a distance of only a few inches. The manner in which the specimens are machined from the block of steel is most important. Any appreciable heating of the steel during machining must be avoided, and such operations as sawing and grinding must be performed very slowly. Experience has shown that far too often extraneous variations of hydrogen content between specimen and specimen have probably been introduced during the preparation of the specimens.

<sup>6</sup> Newell, *Journal of The Iron and Steel Institute*, 1940, No. I, p. 2431.

### Part C.—Determination of Nitrogen

In view of the wide interest in this element and its effects on steel, the methods of analysis reviewed in this part by Dr. Swinden will be particularly valuable. These methods may be divided into two groups:—

(1) Methods in which the nitrogen is liberated as the gaseous element.

(2) Methods in which the nitrogen, after conversion into ammonia, is measured by accepted analytical methods.

The most important of the methods in the first group, practised at the present time, is the vacuum-fusion method of melting the sample in a graphite crucible in a vacuum, whereby the resulting gases are collected and analysed by the conventional methods. The Sub-Committee has amply confirmed the accuracy and wide applicability of this technique to the determination of nitrogen in steel, even in the presence of the more stable nitrides such as chromium, titanium and vanadium.

The most common method of the second group, in which the nitrogen constituent of the steel is converted to ammonia and subsequently measured by conventional chemical methods, consists of solution of the sample in mineral acid, followed by distillation of the ammonia from alkaline solution. If the nitrides present are completely soluble in the acid, the method offers little difficulty, but the voluminous literature of the last 60 years would suggest that such is not always the case. In fact, much of this work has dealt with the necessity for obtaining complete decomposition of the nitrides, or nitrogen-bearing compounds, by modification of the original solvent.

The general applicability and possible sources of inaccuracy of the vacuum-fusion method for the determination of nitrogen in iron and steel are discussed by Dr. Swinden in a sub-section. Reference is made to certain difficulties, but, it is added, the results obtained compare favourably with those obtained by the chemical method when the latter is operated under the best conditions. In fact, results obtained for nitrogen by vacuum fusion have indicated possible errors in commonly accepted chemical methods of determination.

In another sub-section Dr. Swinden discusses the chemical distillation method, and gives a brief outline of the development and modifications in procedure recommended, and compares the results obtained by co-operators using different procedures on typical alloy steels. The influence of certain alloying elements, and of the physical condition of the sample on the simpler solution method, is demonstrated and discussed. A tentative standard method is described together with notes and recommendations; the procedure includes the established distillation over caustic soda, and detailed comments on the blank troubles attendant on this method.

Of considerable interest are the views expressed on the future development of chemical methods. It is stated that the chemical method can be sub-divided into two main operations: (a) The decomposition of the sample; (b) the collection and measurement of the ammonia.

The bulk of previous work has been directed towards obtaining more complete decomposition of the sample, and in the Sub-Committee's experience many of the more-involved procedures, such as initial solution in dilute acid followed by filtration through asbestos and digestion of the residue in mixtures of high-boiling-point

acids, are unnecessary. For most steels the same object can be achieved by digestion of the original sample in sulphuric acid. It must, however, be pointed out that with highly complex alloys separate treatment of an acid-insoluble residue may be necessary and is in fact desirable.

The method of collection and measurement of the ammonia is likely to afford scope for improvement. Whilst the principle of normal distillation over caustic soda has been the standard practice for many years, recent investigators<sup>7</sup> have proposed a steam distillation which considerably reduces the time required for the complete removal of the ammonia. Whilst this will effect some saving of time, it is perhaps not of such importance where batch determinations are conducted, since the decreased time of distillation would limit considerably the number of apparatus which could be operated by one chemist, and the net improvement would be very small. This method does, however, affect the weight of sample taken, thereby improving the accuracy of the nitrogen determination, in so far as bumping troubles due to increased weight are minimised. It is perhaps on these lines that future development will take place.

Finally, one must not overlook the possibility of the development of a technique whereby the distillation can be entirely omitted, using, for example, a colorimetric principle applicable to nitrogen in the presence of iron and the usual steel elements.

### SECTION III—EXAMINATION OF MATERIALS.

In this section accounts are given of some of the uses to which the various methods of analysis have been put during the examination of ferrous materials, and for the purpose of fundamental investigation. Since much of the work has required the use of a ferrous base material of very low oxygen content, it is appropriate that the first sub-section should give a description of the preparation of this oxygen-free iron, known as N.P.L. iron, Mark 2.

This paper by Mr. Sloman and Mr. Cook describes the experimental technique developed at the National Physical Laboratory for the production of low-oxygen content iron bar. Considerable experience had already been obtained in the Metallurgical Department, National Physical Laboratory, of the preparation of high-purity iron, first on a small scale<sup>8</sup> and later on a large laboratory scale,<sup>9</sup> and the method of deoxidation by treatment with hydrogen in the molten state was well established. Not a great deal of work, however, had been carried out on the subsequent working of the metal into small-diameter bar. The method employed in the present case was based on this past experience, and the starting material—namely, electrolytic iron sheet—was the same, but since small amounts of impurities, other than oxygen, could be tolerated, it was possible to bypass the rather lengthy process of conversion, first to ferrous chloride, then to iron oxide and sponge iron, which had been previously adopted for their removal.<sup>9</sup> It was decided to designate the present iron as "N.P.L. Iron, Mark 2," in order to distinguish it from other oxygen-free iron prepared at the N.P.L. and subjected to the intermediate process outlined above.

<sup>7</sup> Kempf and Alresch, *Archiv für das Eisenhüttenwesen*, 1939-40, vol. 13, p. 419.

<sup>8</sup> Adecock and Bristow, *Proceedings of the Royal Society*, 1935, A, vol. 153, p. 172.

<sup>9</sup> Adecock, *Journal of the Society of Chemical Industry*, 1940, vol. 19, p. 28.

Owing to the method of cooling adopted, the ingots were extremely coarse-grained and very brittle, being unable to withstand any form of cold work. Hot working was therefore essential, and the problem became one of developing a technique for the initial breaking down of the large crystals which would not increase the oxygen content. A detailed account is given of the technique developed.

Further research on the surface-oxygen film on iron and steel is described by Mr. Sloman and Mr. Rooney in a second sub-section. The present contribution is an excellent and concise statement, containing much data of paramount importance to a sound understanding of surface films on metals. The extent of interference, attributed to the surface film, according to the type of sample used in the usual methods for the determination of gases, is carefully stated. The use of milled samples in any oxygen determination is not to be recommended.

The reaction of rimming steels to the residue methods was noted in the Third Report of the Sub-Committee, and a further study of several types of rimming steel is submitted by Mr. Rooney and Dr. Jones in the third sub-section. It was shown by Dr. Swinden and Mr. Stevenson in the Third Report (p. 384 p) that solution in alcoholic iodine at 65° C. gave low oxygen results, owing presumably to attack by the solvent on the basic oxides of iron and manganese contained in the low-carbon rimming steel examined. Mr. Rooney and his collaborator have studied in greater detail the application of the alcoholic-iodine method to rimming steels, and the earlier conclusions are substantially confirmed. It must be emphasised that the difficulty is most acute with rimming steels of low-carbon content and consequent high oxygen, occurring mainly as iron and manganese oxides. With such steels Mr. Rooney has modified the standard procedure and investigated the effect of a heat-treatment of the sample, and, whilst a certain measure of improvement is achieved, further difficulties in the non-decomposition of sulphide and carbide have been encountered. X-ray examination was useful in detecting the presence of manganese sulphide and iron carbide, but did not detect any oxide, although a vacuum-fusion determination on a residue revealed the presence of 0.009% of oxygen (see Appendix).

Dr. Hatfield and Dr. Newell, in the fourth sub-section, describes typical results for the gas contents of the raw materials used in steelmaking processes. Considerable variations in the gas contents are recorded, and their significance is discussed. A diminution of the hydrogen content is achieved by heating ferro-alloys, etc., at 650°-850° C., but this procedure is often accompanied by increased oxidation.

The information derived from the co-operative examination of the oxygen of typical acid and basic slags by the usual methods of determination and reported by Mr. Stevenson and Mr. Speight in the fifth sub-section is most valuable. This investigation shows that our present methods of examination satisfactorily account for the oxygen content of acid silicates, but that with basic inclusions recovery may be incomplete. Although it may indeed be stated that such inclusions do not occur normally in steel, knowledge of the limitations of the present methods for oxygen is advanced substantially by these experiments.

A concise paper jointly by Mr. Gray, Mr. Sanders, Mr. Graham and Mr. Short, in the sixth sub-section, describes the occurrence of elemental silicon in residues

from the aluminium-reduction method when applied to high-silicon iron, and the means adopted to overcome this peculiar interference. In addition to being of considerable scientific interest, this unexpected behaviour of silicon is typical of the small but troublesome features which arise all too frequently when new methods are applied to unusual materials.

Mr. Pearce, in the seventh sub-section, states the position with regard to the oxide inclusions in pig and cast irons, reviewing the evidence presented by microscopic and chemical means.

In a further sub-section the results obtained collaboratively for oxygen, hydrogen and nitrogen in a series of commercial alloy steels are shown and amplified by suitable comments by Dr. Swinden.

The foregoing relates to the examination of cold samples and it is felt that the work which the Sub-Committee set out to do in the establishment of methods has, speaking generally, been completed. It is quite clear, however, that it would be of far greater value to be able to determine the gas content (particularly oxygen and hydrogen) during the process of steel manufacture. It is on this subject that the Sub-Committee will concentrate their efforts in the future. Attention is therefore directed to Section IV, which, it is submitted, lays the basis for future work on the determination respectively of oxygen and hydrogen in liquid steel. The importance is elaborated by Dr. Swinden in the Introduction, and in Section IV (a) he and Mr. Stevenson give an account of their experience in furnace-stage oxygen determination, dealing particularly with the bomb method of sampling, the method of dealing with the sample and some typical results obtained. In Section IV (b) Dr. Hatfield and Dr. Newell deal with the sampling of liquid steel for its hydrogen content. Two new methods, the notched chilled-mould method and the balloon-tube method, are described, and a series of interesting results are reported. The conclusion is drawn that the hydrogen content of small cast-steel samples need bear no relationship to that originally present in the molten steel.

### Vanadium in Low-Alloy High Speed Steels

THE effect of quenching and drawing temperatures on the microstructure, hardness and cutting properties of steels containing 0.94-1.45% carbon, 3.8-4.8% chromium, 0.9-3.5% molybdenum, 1.7-6.7% vanadium, and 1.5-3.3% tungsten, as compared to a vanadium-free steel containing 0.76% carbon, 4.1% chromium, 3.1% molybdenum, and 3.2% tungsten was investigated by Gulyaev.\* The fact that vanadium decreases the stability of austenite in the region of decomposition to pearlite and raises the temperature of minute austenite stability, greatly increases the critical cooling rate. Vanadium speeds up the isothermal decomposition of austenite in the second zone (at 300°). Vanadium raises the martensite point and decreases the amount of residual austenite. It also permits the transformation of residual austenite into martensite and forms carbides which are difficult to dissolve in austenite; diminishes the drop in hardness during drawing; and the addition of 2-3% increases the thermal stability of the steel and improves the cutting properties, and is recommended for low-tungsten high-speed steels.

\* A. P. Gulyaev, *Stal* 11, No. 4, 55-60 (1941); *Chem. Zentr.*, 1942, I, 75.

# The Physical Chemistry of Open-Hearth Slags\*

*A survey of present knowledge of the fundamental physico-chemical relationships governing the constitution and properties of open-hearth slags.*

THE purpose of this paper by Dr. James White is two-fold—first, since progress in this field has been somewhat rapid in recent years, it was thought that an attempt to review and correlate the information now available might be desirable, and, secondly, since the knowledge dealt with is scattered widely, it was considered that it would be a service to bring together this material in a readily accessible form. For this reason a good many diagrams, particularly constitutional and thermal equilibrium diagrams, have been reproduced in the paper. The review is concerned primarily with the chemistry of slag, and no attempt has been made to consider the relationships involved from the point of view of their influence on the metal bath.

The subject is presented under twelve main sub-headings, which include the principal constituents of open-hearth slags; thermal equilibrium diagrams of the slag-forming oxides; the system iron-oxygen; equilibrium in the system iron-oxygen in the presence of other oxides; gas oxidation *via* the slag in the open-hearth furnace; the mineralogical constitution of actual furnace slags, and influences affecting their composition; phase relationships in basic slags; fusibility composition relationships; the viscosities of open-hearth slags; and the chemistry of liquid slag.

The principal oxides occurring in open-hearth slags are CaO, MgO, MnO, FeO,  $Fe_2O_3$ ,  $Al_2O_3$ ,  $P_2O_5$ , and  $SiO_2$ , and a knowledge of the systems formed by these oxides with each other is essential to an understanding of the nature of the slag and of its role in steel-making. In this paper Dr. White discusses and correlates the available data concerning these systems, and gives thermal equilibrium and phase diagrams, where these are available, together with probable forms of some of the, as yet, unknown diagrams suggested on the basis of published information. Particular attention is paid to the equilibria governing the relationships between the oxides of iron and gaseous oxygen on the one hand, and between these oxides and metallic iron on the other. The modifying effects produced by the presence of other oxides on these relationships are also discussed.

On the basis of the data presented, Dr. White discusses the question of the constitution of actual furnace slags and puts forward a tentative scheme of phase assemblages in solidified basic slags, which may serve as a basis for further work on the subject. Fusibility and fluidity relationships in furnace slags are considered in so far as they limit the range of "workable" compositions. The question of the molecular constitution of liquid slags is briefly discussed in the final section, which is reproduced in the following, together with the references appertaining thereto.

## The Chemistry of Liquid Slag

Our present knowledge of the chemistry of liquid slags may be said to be tentative only. Definite evidence concerning their constitution is necessarily harder to obtain for liquid slags than for solid slags, in which the crystalline constituents can usually be identified. There is, however, abundant evidence to suggest that compounds do occur in liquid slags. The investigations by Feild and Royster<sup>1</sup> on the viscosity composition relationships of  $CaO$ – $Al_2O_3$ – $SiO_2$  slags, for instance, showed that decided constitutional influences were operative in their melts. Similar evidence is provided by the slag-viscosity data of Rait and Hay,<sup>2</sup> Rait, M'Millan and Hay,<sup>3</sup> Preston,<sup>4</sup> McCaffery<sup>5</sup> and others. In addition, purely chemical evidence is forthcoming, as it is difficult to explain the stabilising effect of CaO on  $P_2O_5$ , CaO on  $Fe_2O_3$  and  $SiO_2$  on FeO in liquid slags without assuming that stable compounds involving these oxides are formed. Many statements are to be found in the literature as to the probable compounds occurring, but often these are little more than mere assumptions with little evidence to support them. Coleclough<sup>6</sup> early tried to group the oxides found in basic slags into stable combinations in an endeavour to provide a rational explanation for the behaviour of such slags in the furnace. He concluded that the CaO combined primarily with the  $P_2O_5$  and  $SiO_2$  to form  $4CaO.P_2O_5$  and  $2CaO.SiO_2$ , respectively, while CaO in excess of the amount required for this combined with  $Fe_2O_3$  to form calcium ferrites. Only if the CaO content of the slag was low could appreciable manganese silicate be formed. He states that the action of CaO in displacing MnO from manganese silicate in basic slags is exactly analogous to its action in acid slags, in which it displaces FeO from ferrous silicate. Krings and Schackmann<sup>7</sup> have concluded that it is the metasilicates of CaO, MnO and FeO that occur in liquid slags, their stabilities decreasing in that order. Tammann and Oelsen,<sup>8</sup> on the other hand, concluded that  $2CaO.SiO_2$  was the most stable silicate in basic slags.

More recently an attempt has been made by the author<sup>9</sup> to show that relationships observed in the study of  $Fe_2O_3$  dissociation equilibria in liquid melts could be

1 Field and Royster. *U.S. Bureau of Mines, 1918, Technological Paper No. 189.*

2 Rait and Hay. *Journal of the Royal Technical College, Glasgow, 1938, vol. 4, p. 252.*

3 Rait, M'Millan and Hay. *Journal of the Royal Technical College, Glasgow, 1939, vol. 4, p. 449.*

4 Preston. *Transactions of the Society of Glass Technology, 1938, vol. 22, p. 45.*

5 McCaffery, Loritz, Goff, Oerterle and Fritsche. *American Institute of Mining and Metallurgical Engineers, 1931, Technical Publication No. 383.*

6 Coleclough. *Journal of The Iron and Steel Institute, 1923, No. 1, p. 262.*

7 Krings and Schackmann. *Zeitschrift für anorganische Chemie, 1932, vol. 206, p. 337.*

8 Tammann and Oelsen. *Archiv für das Eisenhüttenwesen, 1931–32, vol. 5, p. 75.*

9 White. *The Iron and Steel Institute, Carnegie Scholarship Memoirs, 1938, vol. 27, p. 1.*

accounted for with reasonable accuracy on the basis of the simple law of mass action if it were assumed that the melts could be regarded as ideal solutions in one or another of various compounds known to exist in solid slags, these compounds being, however, in general, partially dissociated into their constituent oxides. It was found that the curves for pure iron-oxide melts could be reproduced quite closely on the assumption that  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_4$  were all present in the melts, the relationships between them being conditioned by the reversible reactions:—

$$\text{Fe}_2\text{O}_3 = 2\text{FeO} + \frac{1}{2}\text{O}_2, \text{ whereby } k_1 = \frac{(\text{FeO})^2 \sqrt{\text{O}_2 \text{ Pressure}}}{(\text{Fe}_2\text{O}_3)}$$

$$\text{and } \text{Fe}_2\text{O}_4 = \text{FeO} + \text{Fe}_3\text{O}_4, \text{ whereby } k_2 = \frac{(\text{FeO}) \times (\text{Fe}_3\text{O}_4)}{(\text{Fe}_2\text{O}_4)}$$

where all concentrations are expressed as molar fractions. (Actually, three equations linking the three oxides of iron can be written, but any two of these are sufficient to define the equilibrium completely.) In similar fashion the effect of  $\text{CaO}$  on the dissociation of  $\text{Fe}_2\text{O}_3$  could be accounted for on the assumption that  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  were formed in the melts. The effect of  $\text{SiO}_2$ , on the other hand, was due principally to the formation of  $\text{FeO} \cdot \text{SiO}_2$ ,  $2\text{FeO} \cdot \text{SiO}_2$  being almost entirely dissociated, while with  $\text{CaO}$  and  $\text{SiO}_2$  together in the melts the primary tendency was to form  $\text{CaO} \cdot \text{SiO}_2$  and to a lesser extent  $2\text{CaO} \cdot \text{SiO}_2$  (the latter compound being more highly dissociated than the former). By application of the dissociation constants thus evaluated to established data on the influence of slag composition on slag-metal equilibria it was found possible to evaluate dissociation constants for the manganese silicates and also to show that the observed variations in the slag-metal constants could be reasonably well explained in terms of the concept of slag constitution thus developed. The results obtained indicate that  $\text{CaO} \cdot \text{SiO}_2$ ,  $\text{MnO} \cdot \text{SiO}_2$  and  $\text{FeO} \cdot \text{SiO}_2$  are the principal silicates occurring in liquid slags. The stabilities of these compounds decrease in the order given,  $\text{MnO} \cdot \text{SiO}_2$  being slightly and  $\text{FeO} \cdot \text{SiO}_2$  markedly less stable than  $\text{CaO} \cdot \text{SiO}_2$ . Hence,  $\text{CaO}$  can readily replace  $\text{FeO}$  from combination with  $\text{SiO}_2$ —e.g.,  $\text{CaO}$  additions to acid slags will set free an appreciable proportion of the combined  $\text{FeO}$ .  $\text{MnO} \cdot \text{SiO}_2$  is much less affected by the presence of  $\text{CaO}$ , but in basic slags in which the  $\text{CaO}$  is considerably in excess of the  $\text{MnO}$  little  $\text{MnO} \cdot \text{SiO}_2$  should be present.

The utilisation of slag-metal equilibrium data to throw light on the question of slag constitution is based on the following considerations:—It can be assumed that the relationships between slag and metal are governed, to a fairly close approximation at least, by the ideal solution laws. Thus, the distribution of  $\text{FeO}$  between the two media is known to be according to the partition law, while it has also been possible to evaluate equilibrium constants for the various slag-metal reactions. In practice, however, all such constants are usually expressed in terms of the total weight percentages in the slag and metal of the reactants involved. Mass-action requirements, of course, stipulate that only concentrations of chemically free reactants should be considered in evaluating equilibrium constants, but it is not generally possible to do this for slag and metal reactions, as there is no direct way of determining what

proportion of any reactant is free. Only the total concentrations as got from chemical analysis are available. Hence, only when no compound formation is possible in the slag—e.g., when it is composed of basic oxides only, will the constants so evaluated be true mass-action constants. (It is assumed as a working hypothesis that none of the reactants in the metal phase forms compounds.) When acid oxides are also present in the slags (assuming that stable compounds are formed) these "constants" will no longer be true mass-action constants, and will, in fact, probably have values differing from those for simple basic-oxide slags. This is, of course, found to be the case. The  $\text{FeO}$  partition coefficient (denoted by the symbol  $L_{\text{FeO}}$  and expressed commonly as  $[\text{O}] / (\text{FeO})$  (where the round brackets indicate the concentration in the slag, and the square brackets the concentration in the metal), is appreciably smaller for acid than for basic slags. This is in keeping with the view that all of the  $\text{FeO}$  in acid slags is not chemically free. A similar difference is found in the case of the slag-metal equilibrium constant for the manganese reaction—viz:—

$$K_{\text{Mn}} = \frac{(\text{FeO})[\text{Mn}]}{(\text{MnO})}$$

If this difference is wholly due to the presence of silicates of  $\text{FeO}$  and  $\text{MnO}$  in the acid slag, then, presumably, the true mass-action values of  $L_{\text{FeO}}$  and  $K_{\text{Mn}}$  will be the same for both types of slag. In applying these conclusions to the case of equilibrium between the metal and an acid slag, we can write:

$$(\text{FeO}) = \frac{[\text{O}]}{L_{\text{FeO}}},$$

where  $(\text{FeO})$  is the concentration of free  $\text{FeO}$  in the slag,  $[\text{O}]$  is the concentration of oxygen in the metal, and  $L_{\text{FeO}}$  is the true value of the partition coefficient. Thus, the concentration of free  $\text{FeO}$  in the slag can be calculated. From this, in turn ( $\text{MnO}$ ), the concentration of the free  $\text{MnO}$  in the slag, can be got, since:

$$(\text{MnO}) = \frac{(\text{FeO})[\text{Mn}]}{K_{\text{Mn}}}$$

where  $[\text{Mn}]$  is the concentration of manganese in the metal, and  $K_{\text{Mn}}$  is the true value of the manganese constant. The amounts of  $\text{FeO}$  and  $\text{MnO}$  combined as silicates are obtained by difference, and it is then possible, by trial, to evaluate the dissociation constants of the silicates.

The above forms the basis of the method used by H. Schenck and his co-workers to study the constitution of acid and basic furnace slags.<sup>10, 11</sup> Starting with the former type of slag, they evaluated dissociation constants for the silicates, and then used the information thus obtained to elucidate the more complex constitution of the basic slag. Their conclusions differ somewhat from those described above; for instance, they deduce that the orthosilicates of manganese and iron are the principal silicates occurring in acid slags. In basic slags they find evidence for the existence of calcium silicates (probably the metasilicate chiefly), calcium ferrites (of which the compound  $\text{CaO} \cdot \text{Fe}_2\text{O}_4$  is probably the most important), calcium phosphates (probably the tetraphosphate mainly) and manganese and iron orthosilicates. All of these compounds are partially

(Continued on page 248)

<sup>10</sup> H. Schenck and Brüggemann. *Archiv für das Eisenhüttenwesen*, 1935-36, vol. 9, p. 513.

<sup>11</sup> H. Schenck and Ries. *Archiv für das Eisenhüttenwesen*, 1935-36, vol. 9, p. 589.

# The Strain-Ageing of Killed Low-Carbon Steel

By A Special Correspondent

*Many investigations have been made with a view to the determination of the causes of changes in the mechanical properties of steels that occur spontaneously with the passage of time after some kind of cold deformation. This phenomenon, known as strain-ageing, causes pressing difficulties, and efforts have been made to produce non-ageing steels that will overcome these difficulties. Reference is made to some of the work done, but particular attention is directed to some recent work on the subject which deals with the use of aluminium and particularly with titanium in killed low-carbon steels.*

MUCH work has been carried out on steel with the object of seeking information on the change in mechanical properties that occurs spontaneously with the passage of time, at either ordinary or elevated temperatures, after some kind of cold deformation. This phenomenon, known as strain-ageing, frequently leads to difficulties in pressing components from sheet or strip, especially under normal production conditions when some time may elapse between the rolling of the sheet and its use in the press-shop. An additional difficulty is the fact that the ageing properties of different batches of sheet may vary considerably. To overcome these difficulties, so-called non-ageing steel has been made in large tonnages by the use of aluminium and by careful heat-treatment, but the product has not always been entirely satisfactory.

The subject of strain-ageing of some low-carbon steels has been considered by Edwards, Jones and Walters,<sup>1</sup> and by Edwards, Phillips and Jones.<sup>2</sup> In the former the authors reported the results of an investigation on the influence of cold-work produced by tensile strains, followed by ageing at 250° C., upon the tensile properties of mild steel. Particular consideration was given to the effects of small amounts of cold work, such as are normally produced at the yield stress of normalised materials, and subsequent ageing upon the newly acquired yield-point. It was found that the yield-point after age-hardening is proportional to the yield-point of the material in the original condition. The possible influence of oxygen on strain-age hardening was considered, but all the evidence indicated that this element has no effect when the specimens are strained under pure tensile stresses and aged at temperatures of, say, 250°-300° C. An extension of this investigation, reported by the author, given in the second reference, concerns a study of the influence of some special elements upon the strain-ageing characteristics of low-carbon steels. It was found that the elements studied could be divided into two main groups—viz., those which show little or no tendency to combine with the carbon present in steel, such as aluminium, copper and nickel; and those which

show definite tendencies to form carbides, such as molybdenum, manganese, chromium, vanadium, niobium and titanium. The former increase and the latter diminish the extent of strain-age-hardening of low-carbon steels. From this work it would seem that when sufficient of one of the elements of the second group is added to combine with all the carbon present the material does not strain-age-harden.

Hayes and Griffis<sup>3</sup> claimed that titanium, as well as aluminium, was useful for making non-ageing steel. They showed that the ageing tendency of low-carbon steel containing titanium was eliminated when treated by normalising followed by at least 3 hours annealing at 650° C. and slow cooling. The ageing tendency being determined by means of the tensile stress-strain curve after straining and ageing, such a curve showing a marked break at the yield-point in the ageing steels, but being smooth in the non-ageing steels, the same as directly after straining. Because of this lack of recurrence of the yield-point, non-ageing steel does not suffer from "stretcher strains" in cold-formed sheets, and is, therefore, desirable for stamped or drawn parts.

The cause of strain-ageing in low-carbon steels has been variously ascribed to oxygen, to nitrogen, or to carbon, and no general agreement on this question has yet been reached. Although progress has been made in the manufacture of non-ageing steel, the problem is still complex. Disagreement as to the cause of strain-ageing may be due to the use of different methods of testing adopted by investigators. In addition to the yield-point method,<sup>4, 5, 6</sup> loss by impact resistance,<sup>6, 7, 8</sup> increase in Brinell hardness values,<sup>9</sup> and decrease of damping capacity,<sup>10, 11</sup> have been used for determining ageing.

A more recent contribution to this problem is that of Comstock,<sup>4</sup> who makes particular reference to a study

<sup>3</sup> A. Hayes and R. O. Griffis, "Non-Ageing Iron and Steel for Deep Drawing," *Metals and Alloys*, vol. 5, No. 5, May, 1934, p. 110.

<sup>4</sup> G. F. Comstock, Amer. Soc. Testing Materials, 1943. (Preprint 27.)

<sup>5</sup> B. N. Daniloff, R. F. Mehl, and C. H. Herty, Jr., "The Influence of Deoxidation on the Ageing of Mild Steels," *Transactions Am. Soc. Metals*, vol. 24, No. 3, September, 1936, p. 595.

<sup>6</sup> W. Eilender, H. Cornelius, and H. Knuppel, "Influence of Nitrogen and Oxygen upon Mechanical Ageing of Steel," *Archiv. für das Eisenhüttenwesen*, vol. 8, p. 507 (1935).

<sup>7</sup> H. W. Graham and H. K. Work, "A Work-Brittleness Test for Steel," *Proceedings Am. Soc. Testing Mats.*, vol. 39, p. 571 (1939).

<sup>8</sup> A. B. Kinzel, "The Specification of the Weldability of Steels," *Welding Research Supplement, Journal Am. Welding Soc.*, vol. 6, No. 10, October, 1941, p. 483.

<sup>9</sup> S. A. Saveur and J. L. Burns, "A Method for Studying Strain Hardening Susceptibility and Ageing after Cold Work Deformation," *Metals and Alloys*, vol. 4, No. 1, January, 1933, p. 6.

<sup>1</sup> C. A. Edwards, H. N. Jones, and B. Walters, "A Study of Strain-Age Hardening of Mild Steel," *Journal Iron and Steel Institute* (London), vol. 139, No. 1, p. 341 P (1939).

<sup>2</sup> C. A. Edwards, D. L. Phillips, and H. N. Jones, "The Influence of Some Special Elements upon the Strain-Ageing and Yield-point Characteristics of Low-Carbon Steels," *Journal Iron and Steel Inst.* (London), vol. 142, No. 2, p. 199 P (1940).

of the effect of titanium on the strain-ageing of killed low-carbon steel. Six different methods of testing for susceptibility to strain-ageing were used in this work, as follows:—

1. Automatic plotting of the load-deformation diagram of a tension test, with a specimen first adequately strained, and then tested after a definite period of ageing. The elongation at the yield-point is an indication of the amount of ageing.<sup>2, 3, 5</sup>

2. Determining first the stress required for 5% strain, and after a period of ageing, determining the yield strength. The amount by which the latter exceeds the former is a measure of ageing.<sup>2</sup>

3. Determining the Izod impact resistance of a specimen strained in tension 5%, first directly after straining, and secondly after a period of ageing. A decrease is evidence of strain-ageing.<sup>5, 6, 8</sup>

4. The work-brittleness test, involving Izod impact test of specimens strained by cold drawing through a die.<sup>7, 10</sup> Using a tapered specimen, the amount of strain is varied, and the ageing factor may be introduced between straining and impact testing.

5. Measuring the Rockwell hardness of Brinell impressions, some immediately, and some after an ageing period. The increase in hardness should be a measure of ageing.<sup>9</sup>

6. Damping records of specimens strained 4% in tension, made 15 mins. and 7 days, respectively, after straining. The decrease in the latter value below the former indicated the degree of ageing.<sup>10, 11</sup>

Methods 1, 2, and 6 were found generally to classify steels in about the same way regarding strain-ageing, while methods 3, 4 and 5 classified them quite differently. These two groups of test methods evidently determine different kinds of strain-ageing, which should be distinguished in any discussion of the subject.

The steels used ranged in analysis from 0.022 to 0.135% carbon, 0.16 to 0.56% manganese, 0.002 to 0.23% silicon, 0.0033 to 0.0196% nitrogen, and also contained about 0.015% phosphorus, about 0.035% sulphur, and up to 0.705% titanium. Manganese and silicon were added to all heats after melting, so that all the steel was killed and the ingots were sound. Titanium was added in the form of 40% low-carbon ferro-titanium containing about 7% of aluminium.

All steels were melted in a basic-lined 17 lb. induction furnace and each heat poured in a single ingot about 2.5 in. square. Most of these ingots were forged to  $\frac{1}{2}$  in. round bars, but some were forged  $\frac{1}{2} \frac{7}{8}$  in. square. When heat-treatment was used the bars were heated before machining. Normalising was for  $1\frac{1}{2}$  to 2 hours at 900° to 930° C., followed by cooling in still air, and annealing was for 6 hours at 626° to 644° C., followed by slow-cooling in the furnace, the higher temperatures being used for the lower-carbon steels.

#### Effect of Aluminium

Data obtained from steels without titanium additions are reported in Table I. Some of these steels were deoxidised merely with manganese and silicon, while in others various amounts of aluminium were also used. These results show that all the aluminium treated steels had a well-marked yield-point, whether normalised or

annealed, in the strained condition after ageing either 3 weeks at room temperature or for 1 hour at 228° C. Thus, aluminium was not found to be effective in eliminating this kind of strain-ageing. In the higher carbon steels, however, such as Nos. 4, 6, and 8, when annealed, strained, and aged at room temperature, the yield-point was definitely less well marked when the steels were deoxidised with aluminium than in similar silicon-deoxidised steels, such as Nos. 2 and 3; and was also less well marked in the higher-carbon steels than in lower-carbon steels similarly treated with aluminium. Thus, under the particular conditions of this investigation, aluminium oxidation was found to reduce the yield-point elongation, although it did entirely prevent the return of the yield-point on ageing after straining. The damping capacity tests also reveal a slight but appreciable effect of the same nature, due apparently to the differences in carbon content.

With the hardness and impact tests reported, the steels deoxidised with aluminium show, with few exceptions, less ageing after straining than those less thoroughly deoxidised. The improvement due to the use of aluminium is especially well marked with the annealed specimens, which supports, in some measure, the reports of other investigators that strain-ageing is prevented by strong deoxidation with aluminium. Such a conclusion should be restricted, however, to the kind of strain-ageing indicated by impact and possibly hardness tests, and is not applicable except in a very limited and incomplete manner to the kind revealed either by damping tests or by the nature of the yield-point, at least in these steels made on a laboratory scale in bar form.

#### Effect of Nitrogen

Some evidence on the effect of nitrogen can be derived from the data in Table I, since steel No. 1 was found to contain 0.012%, steel No. 2 to contain 0.008%, and steel No. 3 to contain 0.011% nitrogen. No correlation can be found between these values and the strain-ageing data in the table, although there is some slight correlation between the data and the manganese and silicon contents. This seems to indicate that deoxidation has more influence on strain-ageing than nitrogen.

The data reported by Comstock<sup>4</sup> in Table II mainly concerns the effect of nitrogen on steels deoxidised with aluminium and containing various amounts of titanium. The data are grouped in such a way as to minimise the effect of variations in titanium content.

The only possible conclusion from the data in Table II is that in these killed steels nitrogen has no effect on strain ageing. This applies both to the kind of ageing shown by the form of the yield point and by the damping tests, as well as by the kind shown by impact tests, but it must be clearly restricted to killed steels, made on a laboratory scale, and with soluble nitrogen contents below 0.015%.

All the steels in Table II are practically non-ageing by impact test methods, but all but one are definitely ageing by the yield point method. The exception, No. 15, shows the least ageing by the damping test method, but the most by the impact test method. Although this steel displayed no yield point when tested in the annealed condition after straining and ageing at room temperature, it had a very definite yield point when not annealed, or even when an annealed specimen was aged for 1 hour at 230° C. Its high carbon content should be noted, and

10 S. L. Case, "Work Sensitivity: Embrittlement by Cold Work," *Metal Progress*, vol. 32, No. 5, November, 1937, p. 669; also "Damping Capacity and Ageing of Steel," *Metal Progress*, vol. 33, No. 1, January, 1938, p. 54.

11 J. T. Norton, "A Torsion Pendulum Instrument for Measuring Internal Friction," *The Review of Scientific Instruments*, vol. 10, March, 1939, p. 77.

this is believed to be the chief reason for the apparent lack of ageing of the annealed specimen at room temperature. Steel No. 20 was somewhat similar, and also Nos. 4 and 6 in Table I.

### Effect of Titanium on Strain Ageing

The chief object of this investigation by Comstock<sup>4</sup> was to check the claim of Hayes and Griffis<sup>3</sup> as to the usefulness of a small titanium content in non ageing steel, and as will have been noted, the results from steel No. 15 seem to support their statement in a limited fashion. Despite many attempts, however, that steel could not be duplicated so as to show similar low-ageing characteristics, steel No. 20 in Table II being one of the nearest approaches although much higher in titanium. As a result of the work of Edwards, Phillips and Jones,<sup>2</sup> however, which showed how high-titanium contents in low-carbon steel would eliminate the yield-point and ageing, Comstock<sup>4</sup> extended his investigation to include steels of a similar nature. The conclusions of that paper were found to be well supported by his results, and with no difficulty in reproducibility. This is indicated by the data on the higher titanium steels in Table III. The results of work-brittleness tests<sup>7</sup> on these steels are reported graphically in Fig. 1.

Table III shows very definitely that only the high-titanium steels with titanium-carbon ratio above 4.5 exhibited no yield-point elongation after straining and ageing, and this is true whether the steels were tested in the normalised or annealed condition, and irrespective of aluminium additions or nitrogen contents. The

TABLE I.  
STRAIN AGEING DATA ON STEELS TREATED WITH DIFFERENT AMOUNTS OF ALUMINIUM.

Steel.	Aluminium Added, per cent.	Chemical Composition, %.				Yield Point Elongation after Ageing, %.	Impact Values, Ft.-lb.				Rockwell B Hardness of Brinell Impression.	Specific Damping, %.					
		Carbon.	Manganese.	Silicon.	Aluminium		Strained in Tension.	Strained by Cold Drawing.	Not Aged.	Aged.		Not Aged.	Aged.	Increase.	Aged 15 Mins.	Aged 7 Days.	Decrease.
NORMALISED SPECIMENS STRAINED 4%: AGED AT 450°F. FOR 1 HOUR.																	
No. 1	0	0.07	0.16	0.11	0.001	3.1	—	—	—	—	86.5	95	8.5	—	—	—	—
No. 2	0	0.10	0.27	0.20	0.001	1.9	—	—	—	—	88.5	96	7.5	—	—	—	—
No. 4	0.05	0.09	0.40	0.22	0.05	2.9	—	—	—	—	87.5	93	5.5	—	—	—	—
No. 6	0.10	0.10	0.42	0.18	0.095	2.2	—	—	—	—	88	92.5	4.5	—	—	—	—
No. 8	0.15	0.09	0.35	0.12	0.14	3.0	—	—	—	—	83.5	91	7.5	—	—	—	—
NORMALISED SPECIMENS STRAINED 5 TO 7%: AGED AT ROOM TEMPERATURE FOR 3 WEEKS.																	
No. 3	0	0.09	0.52	0.19	—	—	—	—	12.5	116.5	—	—	—	—	—	—	—
No. 5	0.05	0.05	0.36	0.09	—	1.1	—	—	135	137	—	—	—	—	—	—	—
No. 7	0.10	0.06	0.42	0.11	—	1.1	—	—	135	130	—	—	—	—	—	—	—
No. 9	0.15	0.04	0.31	0.07	—	1.1	—	—	130	137.5	—	—	—	—	—	—	—
NORMALISED AND ANNEALED SPECIMENS STRAINED 5 TO 8%: AGED AT 450°F. FOR 1 HOUR.																	
No. 1	0	0.07	0.16	0.11	0.001	2.5	88	98	—	—	85.5	88.5	8.5	—	—	—	—
No. 2	0	0.10	0.37	0.20	0.001	2.5	115	114	—	—	83.5	90.5	7	—	—	—	—
No. 3	0	0.09	0.52	0.19	—	1.7	—	—	—	—	83	90.5	7.5	—	—	—	—
No. 4	0.05	0.09	0.40	0.22	0.05	1.1	115	123	—	—	86	87	1	—	—	—	—
No. 5	0.05	0.05	0.36	0.09	—	1.5	134	138	136	132.5	—	—	—	—	—	—	—
No. 6	0.10	0.10	0.42	0.18	0.095	1.1	116	123	—	—	85	87.5	2.5	—	—	—	—
No. 8	0.15	0.09	0.35	0.12	0.14	1.5	120	123	—	—	83.5	81.5	—	—	—	—	—
NORMALISED AND ANNEALED SPECIMENS STRAINED 4 TO 7%: AGED AT ROOM TEMPERATURE FOR 3 WEEKS. <sup>a</sup>																	
No. 1	0	0.07	0.16	0.11	0.001	1.6	94	38	—	—	85.5	91.5	6	—	—	—	—
No. 2	0	0.10	0.37	0.20	0.001	1.5	117	120	—	—	78	85	7	6.5	1.4	5.15	—
No. 3	0	0.09	0.52	0.19	—	1.45	—	—	132	135	85.5	83.5	—	—	—	—	—
No. 4	0.05	0.09	0.40	0.22	0.05	0.45	127	123	—	—	84	83.5	—	7.5	2.9	4.6	—
No. 5	0.05	0.05	0.36	0.09	—	1.5	134	138	136	132.5	—	—	—	7.8	1.6	6.2	—
No. 6	0.10	0.10	0.42	0.18	0.095	1.1	116	123	—	—	85	82	—	7.7	3.7	4.0	—
No. 7	0.10	0.06	0.42	0.11	—	1.4	138	140	130.5	139	—	—	—	8.1	1.5	6.6	—
No. 8	0.15	0.09	0.35	0.12	0.14	0.8	120	123	—	—	84.5	84.5	—	7.75	2.8	4.95	—
No. 9	0.15	0.04	0.31	0.07	—	1.6	136	137	125.5	135	—	—	—	8.0	1.4	6.6	—

<sup>a</sup> Ageing for the damping test was for only one week.

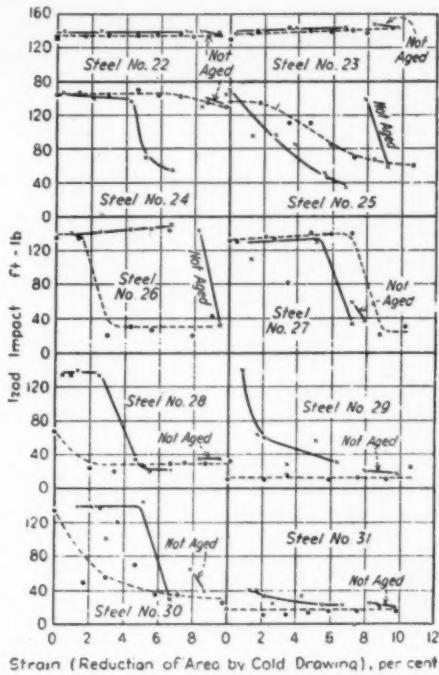


Fig. 1.—Work-brittleness tests of titanium steels.  
Full lines represent normalised specimens aged 3 weeks, except right-hand ends, which are not aged. Dotted lines represent normalised and annealed specimens aged 3 weeks.

damping tests also showed those steels to be practically non-ageing in comparison to the lower-titanium steels. These characteristics were evidently governed by the titanium-carbon ratio; and whether this ratio was very low or just below 4.5 made little difference. The change in ageing susceptibility was thus not a gradual change in the series of steels, but occurred sharply as the titanium-carbon ratio rose to 4.8 or higher.

None of these steels showed appreciable ageing by the impact test method, but some of the high-titanium steels gave low impact values only when not aged, and had excellent impact resistance after ageing; steels Nos. 29 and 31, however, gave no high impact values, and it is interesting to note that these two showed slightly more ageing by the damping test than the other four high-titanium steels. The ferrite grain sizes of the specimens were

TABLE II.  
STRAIN AGEING DATA ON ALUMINIUM-DEOXIDISED STEELS WITH DIFFERENT NITROGEN CONTENTS.

Steel.	Aluminium Added, %	Chemical Composition, %						Yield Point Elongation after Ageing, %	Impact Values, ft.-lb						Specific Damping, %, Normalised and Annealed.				
		Carbon.	Manganese.	Silicon.	Titanium.	Soluble	Nitrogen.		Normalised Only.	Normalised & Annealed.	Strained in Tension, Normalised and Annealed.	Strained by Cold- Drawing.	Normalised Only.	Normalised and Annealed.	Not Aged.	Aged.	Not Aged.	Aged.	
SPECIMENS STRAINED 4 TO 7%: AGED AT ROOM TEMPERATURE FOR 3 WEEKS. <sup>a</sup>																			
No. 7	0.10	0.04	0.42	0.11	—	0.0040	0.0040	1.2	1.4	138	140	125	130	131	131	8.1	1.5	6.6	
No. 5	0.05	0.05	0.36	0.09	—	0.0066	0.0066	1.1	1.5	134	138	135	137	136	138	7.8	1.6	6.2	
No. 10	0.05	0.06	0.42	0.10	—	0.0145	0.0149	1.3	1.3	137	142	141	143	133	142	6.5	1.2	5.3	
No. 11	0.10	0.05	0.40	0.11	—	0.0149	0.0153	1.3	1.5	140	145	142	143	134	142	7.2	1.4	5.8	
Steel with no Titanium																			
No. 12	0.05	0.04	0.36	0.09	0.068	0.029	0.0033	1.6	1.7	141	140	139	137	131	135	7.4	1.9	5.5	
No. 13	0.15	0.05	0.32	0.07	0.090	None	0.0062	1.8	1.6	142	142	140	139	142	149	7.7	1.9	5.8	
No. 14	0.10	0.05	0.43	0.15	0.108	0.0011	0.0069	1.6	1.5	143	147	147	145	144	153	6.3	1.2	5.1	
No. 15	0.05	0.12	0.43	0.22	0.069	0.0049	0.0087	1.2	0	131	123	—	—	—	—	7.0	4.3	2.7	
No. 16	0.10	0.05	0.42	0.14	0.112	0.0049	0.0122	1.6	1.3	135	140	136	140	141	141	6.7	1.6	5.1	
No. 17	0.15	0.06	0.38	0.10	0.100	0.0008	0.0141	1.6	1.4	142	145	143	147	138	145	6.9	1.4	5.5	
No. 18	0.05	0.06	0.50	0.17	0.045	0.0090	0.0196	1.6	1.1	140	145	140	138	150	143	5.3	1.8	3.5	
Steel with low Titanium																			
No. 19	0.05	0.07	0.41	0.19	0.213	0.0011	0.0045	2.0	1.7	143	153	150	151	155	157	5.2	1.2	4.0	
No. 20	0.10	0.10	0.40	0.20	0.188	0.0046	0.0107	—	0.6	—	149	150	152	155	—	—	—	—	—
No. 21	0.05	0.06	0.49	0.20	0.202	0.0021	0.0176	—	1.4	—	163	153	158	160	—	—	—	—	—
Steel with Higher Titanium																			
No. 15	0.05	0.12	0.43	0.22	0.069	0.0049	0.0087	2.1	1.3	113	125	—	—	—	—	—	—	—	
No. 20	0.10	0.10	0.40	0.20	0.188	0.0046	0.0107	—	1.3	—	—	—	—	—	—	—	—	—	
No. 21	0.05	0.06	0.49	0.20	0.202	0.0021	0.0176	—	1.4	—	—	—	—	—	—	—	—	—	
SPECIMENS STRAINED 5 TO 8%: AGED AT 450° F. FOR 1 HOUR.																			

<sup>a</sup> Ageing for the damping tests was only for one week.

determined to throw light on the variations in impact results, and all the high titanium steels were found to be coarser grained than the low titanium steels that had distinct yield-points. Their impact values, however, could not be correlated with the grain size.

The work brittleness tests reported in Fig. 1 show rather irregular results. Steels Nos. 24 and 25, with titanium-carbon ratios just below the critical value, and possibly No. 30, are the only steels that seem to exhibit ageing by this test. These curves prove that many steels may give good impact values and apparently no ageing after only 2% strain, while the results may be entirely different by the impact method of testing for strain-ageing if 5% or more strain is applied.

The results reported in Table III were checked by slightly different tests on a few additional steels of

similar nature, and these later results are shown in Table IV. In this work straining only 2% and ageing 16 hours at 200° C. was tried, as has been specified by Kinzel<sup>8</sup> for determining strain-ageing, but was found to be definitely unsatisfactory, not only for straining by cold-drawing, but also for tensile straining. The entire gauge length of many tension test specimens was not deformed when the strain was restricted to only 2% elongation, so that part of it remained in the unstrained condition and would, therefore, show a yield-point after ageing even if the steel were actually of non-ageing character.

The results in Table IV support those previously reported in indicating practically non-ageing quality in those steels having a titanium-carbon ratio above 5. Steel No. 35 seems in a slight degree exceptional, but the 0.2% yield-point elongation found on ageing at high temperature was barely appreciable and may perhaps be considered as within the experimental error. Less than 2% increase in yield strength due to ageing is also probably negligible and within the experimental error. Steel No. 32 shows considerable strain-ageing by every method, in spite of a small titanium content, but its low manganese and silicon content indicate that it was probably more highly oxidised in melting than the other steels. The comparison of this steel with the others in Table IV furnishes additional support to the conclusion that deoxidation is important in preventing strain-ageing of the kind revealed by impact and hardness tests, but steel No. 33 shows that it is not sufficient for preventing the kind of strain-ageing shown by the yield-point methods.

### Effect of Titanium on the Tensile Properties

Further tests were carried out to determine whether titanium above 4.5 times the carbon content would not eliminate the yield-point of steel even if it were not heat-treated or strained, and also if the carbon content were somewhat higher than in the titanium steels tested so far. Another point of interest was the effect of soaking the ingots at a high temperature, as would be done in large-scale commercial practice, on the yield-point and

TABLE III.  
STRAIN AGEING DATA ON TITANIUM STEELS STRAINED ABOUT 5% AND AGED AT ROOM TEMPERATURE.

Steel.	Aluminium Added, %	Chemical Composition, %						Yield Point Elongation after Ageing, %	Impact Value after Straining in Tension, Ft.-lb., Normalised and Annealed.	Ferrite grains per square millimetre in Impact	Specific Damping, %,	
		Carbon.	Manganese.	Silicon.	Nitrogen.	Titanium.	Ratio, Titanium to Carbon.					
No. 22	0	0.06	0.40	0.08	0.0103	0.090	1.5	1.3	1.3	125	127	1,198
No. 23	0	0.04	0.38	0.12	0.0046	0.086	1.1	1.6	1.6	140	145	1,105
No. 24	0.10	0.06	0.47	0.13	0.0137	0.246	4.1	1.3	1.6	148	148	650
No. 25	0	0.05	0.45	0.10	0.0108	0.210	4.2	1.8	0.5	145	130	75
No. 26	0.10	0.05	0.47	0.17	0.0052	0.240	4.8	0	0	37	145	125
No. 27	0	0.14	0.40	0.15	0.0054	0.210	5.2	0	0	145	145	180
No. 28	0	0.01	0.39	0.14	0.0055	0.255	6.4	0	0	146	146	145
No. 29	0.10	0.03	0.45	0.13	0.0060	0.230	6.6	0	0	12	19	175
No. 30	0.10	0.07	0.46	0.17	0.0043	0.330	6.6	0	0	36	147	115
No. 31	0	0.04	0.42	0.09	0.0099	0.200	7.5	0	0	41	36	85

ageing properties of the high-titanium steels. For this purpose two additional series of titanium steels were made, both series including steels of 0.12 to 0.135% carbon as well as of lower carbon. One series of ingots was heated as usual to about 960° C. before forging, and the other series was soaked for several hours at about 1,070° C. according to usual soaking-pit practice. The analysis of these steels are given in Table V. The aluminium additions vary because all the ingots were not made at the same time, but in titanium steels such variations in aluminium treatment are of minor importance, as far as the properties of the steel are concerned, and may safely be disregarded here.

The ingots were forged to in. round bars and all were finished at about the same temperature. Only tension specimens were made from these bars, and all

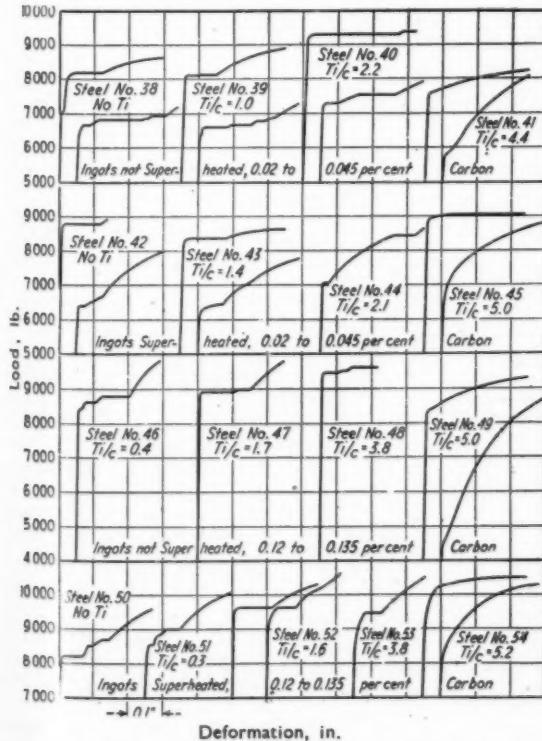


Fig. 2.—Load-deformation diagrams of as-forged specimens.

Where two curves are shown for the same steel, the upper left one represents a strained and aged specimen. The other curves represent specimens without previous straining.

TABLE IV.  
STRAIN AGEING DATA ON NORMALISED AND ANNEALED TITANIUM STEELS.

Steel	Chemical Composition, %			Yield Point Elongation after Strain- ing 5% and Ageing, %	Increase in Strength Due to Ageing after Straining 5%, %	Impact Specimens Strained by Cold Draw- ing.		Rockwell B Hardness of Brinell Impression.		
	Ratio, Titanium to Carbon,					Izod Value, ft.-lb.	2% Strain.			
	Carbon,	Manganese	Silicon,			Aged 1 hr. at 450° F.	Aged 16 hrs. at 200° C.			
No. 32	0.07	0.27	0.004	0.5-1.85	1.7-1.2	20.6	23.4	12.4		
No. 33	0.05	0.43	0.13	2.0-1.25	1.3-1.55	12.2	9.8	12.4		
No. 34	0.04	0.40	0.10	5.3	0	0	9	14.5		
No. 35	0.05	0.44	0.10	5.5-0.2	0.2	0	1.4	14.1		
No. 36	0.03	0.46	0.12	5.8	0	0	1.9	1.5		
No. 37	0.05	0.43	0.14	6.4	0	0	1.5	1.5		
						Aged 1 hr. at 450° F.	Aged 16 hrs. at 200° C.			
						Not Aged.	Not Aged.			
						Aged 3 weeks at 70° F.	Aged 1 hr. at 450° F.			
								Not Aged.		
								Aged 3 weeks at 70° F.		
								Increased.		

TABLE V.  
CHEMICAL ANALYSES OF THE INGOTS USED.

Heated to about 1,750° F. before Forging.						Soaked at About 2,150° F. before Forging.					
Steel,	Alu- minum Added, %	Car- bon,	Manganese,	Silicon,	Titanium,	Steel,	Alu- minum Added, %	Carbon,	Manganese,	Silicon,	Titanium,
No. 38	0.0	0.035	0.42	0.15	None	—	0.10	0.037	0.42	0.13	None
No. 39	0.05	0.032	0.38	0.002	0.033	1.0	0.05	0.022	0.34	0.016	0.032
No. 40	None	0.040	0.20	0.07	0.090	2.2	0.10	0.042	0.15	0.016	0.090
No. 41	0.05	0.044	0.30	0.07	0.195	4.4	0.05	0.041	0.35	0.12	0.207
No. 46	0.05	0.134	0.56	0.14	0.059	0.4	No. 42	0.10	0.124	0.43	0.19
No. 47	None	0.120	0.42	0.23	0.202	1.7	No. 51	0.10	0.126	0.38	0.18
No. 48	0.05	0.131	0.51	0.20	0.495	3.8	No. 52	0.10	0.130	0.38	0.19
No. 49	0.05	0.124	0.46	0.17	0.615	5.0	No. 53	0.05	0.131	0.44	0.13
							No. 54	0.05	0.135	0.50	0.20
											0.705

TABLE VI.  
TENSION TESTS OF AS-FORGED SPECIMENS.

Steel,	Ratio Titanium to Carbon.	Yield Strength (from Fig. 2), psi.	Yield Point by Drop of Beam psi.	Tensile Strength, psi.	Elongation, %.		Reduction of Area, %.
					At Yield Point in 4.5 in.	Total in 6 in.	
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS NOT SUPERHEATED.							
No. 38 ...	0	42,000	42,800	51,700	5.35	24.5	80.5
No. 39 ...	1.0	39,000	40,800	50,300	3.1	25.0	79.8
No. 40 ...	2.2	44,500	44,800	52,100	4.75	25.8	77.1
No. 41 ...	4.4	36,100	—	52,500	0	20.5	87.0
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS SUPERHEATED.							
No. 42 ...	0	40,000	40,000	54,000	1.65	19.5	74.8
No. 43 ...	1.4	40,200	40,200	51,600	1.35	17.8	69.9
No. 44 ...	2.1	44,000	44,000	55,100	6.0	13.3	78.3
No. 45 ...	5.0	41,700	—	56,700	0	15.0	87.0
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS NOT SUPERHEATED.							
No. 46 ...	0.4	55,000	54,600	71,000	3.1	23.0	65.2
No. 47 ...	1.7	58,600	58,600	73,300	3.3	19.7	72.2
No. 48 ...	3.8	57,000	59,700	68,400	3.8+	17.0	79.1
No. 49 ...	5.0	28,500	—	60,000	0	21.0	69.9
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS SUPERHEATED.							
No. 50 ...	0	51,800	52,500	65,200	1.55	16.3	66.0
No. 51 ...	0.3	54,000	54,000	67,000	2.15	13.2	69.8
No. 52 ...	1.6	57,500	61,800	75,100	1.2	14.7	73.6
No. 53 ...	3.8	54,200	60,000	70,900	1.1	12.0	79.1
No. 54 ...	5.2	51,100	—	64,900	0	11.8	77.9

were of the same form and tested in the same way. The two specimens from the upper part of each ingot, below the sink-heat, were tested in the as-forged condition, without heat-treatment. One was not strained before testing, while the other was strained to 5% elongation and then aged before testing. The ageing of the lower-carbon steels, Nos. 38 to 45 inclusive, was for 3 weeks at room temperature, while steels Nos. 46 to 54,

TABLE VII.  
TENSION TESTS OF AS-FORGED SPECIMENS STRAINED AND AGED.

Steel.	Ratio, Titanium to Carbon.	Yield Strength before Straining, psi.	Stress for 5% Strain, psi.	After Straining and Ageing.			Elongation, %.		Reduction of Area, %.
				Yield Strength (from Fig. 2), psi.	Drop of Beam, psi.	Tensile Strength, psi.	At Yield Point in 4.5 in.	Total in 6 in.	
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS NOT SUPERHEATED.									
No. 38	0	46,500	46,500	47,100	54,800	57,400	2.3	16.3	78.9
No. 39	1.0	39,500	43,100	53,500	54,000	59,700	2.1	19.7	73.5
No. 40	2.2	46,500	47,800	55,000	55,500	55,800	5.3	22.0	77.8
No. 41	4.4	34,300 <sup>2</sup>	47,200	50,100	—	55,100	0	27.8	77.5
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS SUPERHEATED.									
No. 42	0	40,000	51,000	58,000	58,600	58,600	2.7+	13.3	74.2
No. 43	1.4	38,800	48,400	57,000	57,800	60,000	2.6	15.2	78.5
No. 44	2.1	52,800	59,600	?	64,600	64,600	?	10.3	77.6
No. 45	5.0	49,800 <sup>2</sup>	57,900	57,800	61,600 <sup>2</sup>	62,100	0	14.7	81.3
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS NOT SUPERHEATED.									
No. 46	0.4	53,800	61,000	72,300	74,200	80,500	3.1	20.2	62.3
No. 47	1.7	59,900	64,300	73,000	75,500	77,600	2.45	15.3	68.6
No. 48	3.8	61,500	62,800	?	77,400	80,000	3.35	16.7	77.7
No. 49	5.0	29,400 <sup>2</sup>	53,500	53,200	56,000	62,700	0.3?	24.2	81.2
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS SUPERHEATED.									
No. 50	0	58,500	63,700	?	76,300	78,100	3.3	15.5	62.1
No. 51	0.3	59,000	64,500	73,300	74,300	74,300	?	10.0	66.7
No. 52	1.6	48,800	49,900	62,100	62,500	67,500	2.4	22.0	70.0
No. 53	3.8	58,300	67,900	?	81,500	81,500	?	13.3	76.5
No. 54	5.2	52,000 <sup>2</sup>	64,000	60,200	67,300 <sup>2</sup>	68,500	0.55	15.8	76.8

containing 0.12 to 0.135% carbon, were aged at room temperature for 3 weeks and also at 230° C. for 1 hour before testing.

The results recorded for the as-forged test specimens are given in Tables VI and VII, and most of the load deformation curves are reproduced in Fig. 2. Those omitted were from strained and aged bars, and were

results are given in Tables VIII and IX, and Fig. 3.

The two specimens from the end of the forged bar made from the bottom of each ingot were normalised 1½ hour at 928° C. and annealed 6 hours at 640° C., followed by slow cooling in the furnace. They were then machined and tested in the same way as the others, one from each ingot without preliminary straining, and the other after straining and ageing. The results are given in Tables X and XI, and Fig. 4.

From the results of this investigation it is concluded that with at least 4.5 times as much titanium as carbon, steels with less than 0.045% carbon, or with 0.12 to 0.135% carbon, have yield strengths generally much lower than similar steels without titanium, and also have better ductility. The difference in tensile strength between the two classes of steel is generally less than the difference in yield strength, and is very much less when tests are made with specimens not previously strained and aged. Furthermore, the high-titanium steels do not have a distinct yield-point whether in the as-forged, normalised, annealed, or aged condition. These characteristics should make

TABLE IX.  
TENSION TESTS OF NORMALISED SPECIMENS STRAINED AND AGED.

Steel.	Ratio, Titanium to Carbon.	Yield Strength before Straining, psi.	Stress for 5% Strain, psi.	After Straining and Ageing.			Elongation, %.		Reduction of Area, %.
				Yield Strength (from Fig. 3), psi.	Drop of Beam, psi.	Tensile Strength, psi.	At Yield Point in 4.5 in.	Total in 6 in.	
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS NOT SUPERHEATED.									
No. 38	0	35,400	40,000	47,800	48,600	57,500	1.4	21.7	77.5
No. 39	1.0	36,600	39,000	48,500	49,600	60,000	1.65	23.7	78.1
No. 40	2.2	34,800	39,600	47,800	49,100	56,300	1.6	25.8	76.8
No. 41	4.4	22,300 <sup>2</sup>	38,600	40,400	41,300	48,400	0.55	27.7	88.9
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS SUPERHEATED.									
No. 42	0	36,400	40,000	47,800	48,600	57,600	1.4	24.0	75.0
No. 43	1.4	28,600	36,200	44,800	46,100	57,000	1.65	25.2	81.2
No. 44	2.1	37,500	38,800	46,000	47,300	54,200	1.55	20.8	75.0
No. 45	5.0	21,100 <sup>2</sup>	36,900	39,100	—	47,000	0	32.2	88.9
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS NOT SUPERHEATED.									
No. 46	0.4	52,100	58,900	71,400	73,500	79,500	3.05	20.5	62.2
No. 47	1.7	45,600	49,700	61,400	62,000	68,000	2.7	20.8	72.9
No. 48	3.8	50,600	58,400	69,800	70,700	79,800	2.3	18.2	78.3
No. 49	5.0	23,600 <sup>2</sup>	48,100	50,600	—	57,800	0	21.3	81.0
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS SUPERHEATED.									
No. 50	0	40,100	48,300	59,200	59,800	69,100	2.1	23.3	65.0
No. 51	0.3	42,800	46,200	53,500	55,000	62,100	1.75	24.0	70.2
No. 52	1.6	46,000	50,100	60,000	60,500	67,000	2.0	22.7	69.8
No. 53	3.8	39,500	50,700	59,000	59,900	73,100	2.05	20.3	79.5
No. 54	5.2	19,800 <sup>2</sup>	44,000	46,000	—	53,000	0	25.8	81.2

TABLE VIII.  
TENSION TESTS OF NORMALISED SPECIMENS.

Steel.	Ratio Titanium to Carbon.	Yield Strength (from Fig. 3), psi.	Yield Point by Drop of Beam psi.	Tensile Strength, psi.	Elongation, %.		Reduction of Area, %.
					At Yield Point in 4.5 in.	Total in 6 in.	
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS NOT SUPERHEATED.							
No. 38 ...	0	35,200	36,300	50,000	4.45	28.0	78.9
No. 39 ...	1.0	33,400	36,100	49,400	4.65	33.3	81.6
No. 40 ...	2.2	34,000	34,100	48,600	4.35	29.2	79.4
No. 41 ...	4.4	33,400	—	48,900	0	9.7	86.1
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS SUPERHEATED.							
No. 42 ...	0	33,000	33,100	49,100	4.45	31.7	79.2
No. 43 ...	1.4	26,200	28,400	46,900	2.7	33.3	85.1
No. 44 ...	2.1	34,000	34,100	48,200	4.05	31.7	79.2
No. 45 ...	5.0	15,500	—	45,000	0	27.0	88.7
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS NOT SUPERHEATED.							
No. 46 ...	0.4	51,000	51,000	69,800	3.9	25.0	69.0
No. 47 ...	1.7	46,000	46,400	59,900	4.4	27.0	73.0
No. 48 ...	3.8	48,200	48,900	66,000	3.5	22.0	81.4
No. 49 ...	5.0	21,000	—	56,300	0	23.2	79.6
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS SUPERHEATED.							
No. 50 ...	0	38,000	38,900	58,800	3.25	28.7	68.1
No. 51 ...	0.3	39,800	40,100	56,200	4.35	28.5	73.0
No. 52 ...	1.6	44,700	44,800	59,400	4.55	26.7	73.1
No. 53 ...	3.8	55,200	55,200	58,000	2.1	24.0	83.9
No. 54 ...	5.2	20,400	—	53,000	0	25.7	83.0

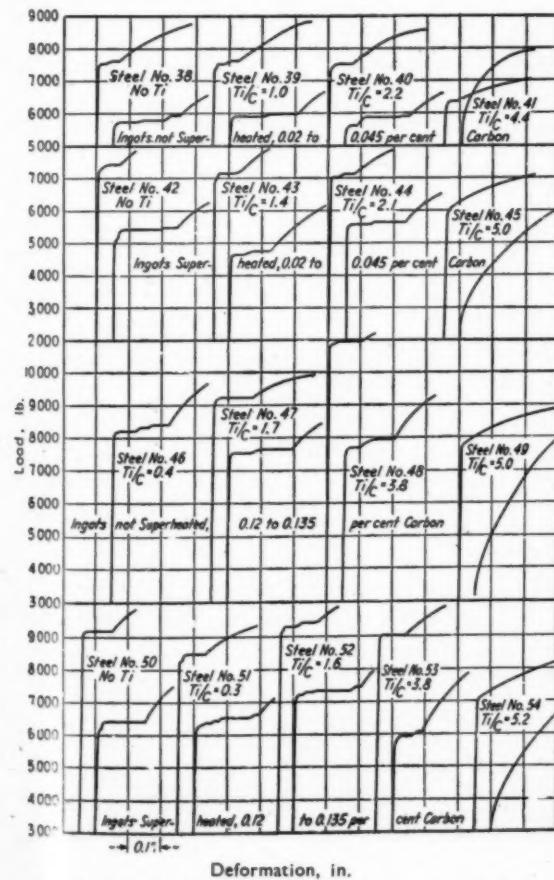


Fig. 3.—Load-deformation diagrams of normalised specimens.

The left curve of each pair represents a strained and aged specimen. The curve to the right, in each pair, represents a specimen not strained before testing.

the high-titanium steels very attractive as a material for sheets that must be formed by deep drawing, since with a low yield strength and high ductility they should be easily formed, and it should be impossible to form "stretcher-strain" markings in them if no definite yield-point occurs.

Another advantage for the high-titanium steel is that annealing does not seem to be necessary. It will be noted by comparing Tables VIII and X, or Tables IX and XI, that all the properties of each class of normalised high-titanium steel compare very favourably with the properties of the corresponding non-titanium steel in the normalised and annealed condition. Since annealing is not required with high-titanium steel to give it a low enough yield strength, or sufficient ductility, or to make it non-ageing with respect to the yield-point, this step might be omitted in processing such sheets with considerable economy.

Since the results obtained with titanium at least 4.5 times the carbon content have been shown to be practically the same with carbon below 0.045% as with carbon from 0.12 to 0.135%, and to agree with results

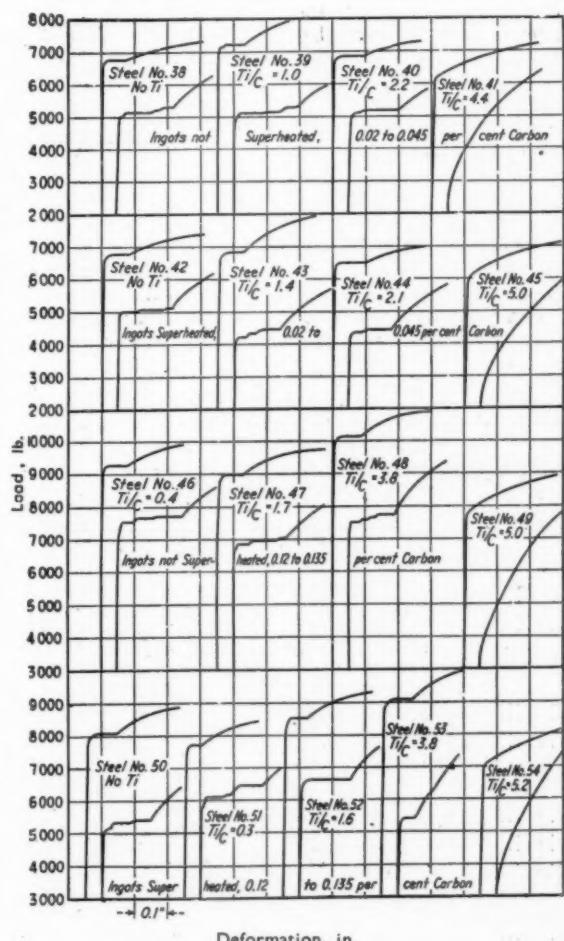


Fig. 4.—Load-deformation diagrams of normalised and annealed specimens.

The left curve of each pair represents a strained and aged specimen. The curve to the right, in each pair, represents a specimen not strained before testing.

that have been reported previously with intermediate carbon contents, there seems little doubt that these conclusions apply generally to all steels with carbon contents at least up to 0.135%.

So far as ageing is concerned, it is obvious that since the high-titanium steels do not have a distinct yield-point even as forged, the absence of change in the character of their yield-points on ageing after straining cannot be used as evidence of non-ageing quality. The data in Tables VII, IX, and XI, however, throw some light on the ageing of these steels by showing the increase in stress value between straining 5% and the yield strength after straining and ageing. Any such increase could only be the result of ageing.

The tension test results reported above confirm the statements by Edwards, Phillips and Jones,<sup>2</sup> that titanium contents sufficient to combine with all the carbon in low-carbon steel not only prevent strain-ageing as shown by the form of the yield-point, but also eliminate the yield-point of the steel. Such steel, with a titanium-carbon ratio above 4.5, seems to be a fundamentally different material from ordinary killed low-carbon steel

TABLE XI.  
TENSION TESTS OF NORMALISED AND ANNEALED SPECIMENS, STRAINED AND AGED.

Steel.	Ratio, Titanium to Carbon.	Yield Strength before Straining, psi.	Stress for 5% Strain, psi.	After Straining and Ageing.			Elongation, %.		Reduction of Area, %
				Yield Strength (from Fig. 4), psi.	Drop of Beam, psi.	Tensile Strength, psi.	At Yield Point in 4.5 in.	Total in 6 in.	
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS NOT SUPERHEATED.									
No. 38 . . . . .	0	33,200	37,300	42,800	43,500	49,100	1.4	33.3	82.6
No. 39 . . . . .	1.0	31,600	37,200	45,900	46,300	53,100	1.8	27.0	81.1
No. 40 . . . . .	2.2	31,400	37,600	43,500	44,300	48,800	2.0	34.3	80.7
No. 41 . . . . .	4.4	18,600	38,300	40,100	—	47,500	0	32.5	87.1
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS SUPERHEATED.									
No. 42 . . . . .	0	32,500	37,400	42,800	43,700	49,700	1.6	33.2	79.9
No. 43 . . . . .	1.4	28,000	34,700	43,100	43,600	52,500	1.65	24.3	80.5
No. 44 . . . . .	2.1	29,000	35,800	41,300	42,000	47,600	2.2	31.7	79.8
No. 45 . . . . .	5.0	18,600	37,600	38,500	—	47,800	0	32.5	88.2
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS NOT SUPERHEATED.									
No. 46 . . . . .	0.4	47,400	52,700	59,300	59,700	64,800	1.55	22.3	67.6
No. 47 . . . . .	1.7	42,500	50,200	56,700	57,500	63,300	1.5	25.7	75.0
No. 48 . . . . .	3.8	46,700	56,300	65,400	66,000	71,100	1.8	17.2	79.0
No. 49 . . . . .	5.0	22,200	48,500	50,500	—	58,000	0	18.8	77.5
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS SUPERHEATED.									
No. 50 . . . . .	0	33,800	42,800	51,500	52,200	58,000	1.95	20.3	71.2
No. 51 . . . . .	0.3	38,400	43,800	48,600	49,500	56,600	1.0	31.0	74.2
No. 52 . . . . .	1.6	41,900	48,200	54,000	54,600	61,000	1.3	25.7	74.4
No. 53 . . . . .	3.8	33,800	49,000	57,700	58,500	64,900	1.75	19.3	80.6
No. 54 . . . . .	5.2	18,600	43,800	46,000	—	55,000	0	25.3	81.3

or steel treated with small amounts of titanium or aluminium or both. In yield characteristics it resembles a non-ferrous alloy. This is true of the steel in the as-forged condition as well as after heat-treatment, whether superheated before forging or not. It also applies to steels with any carbon content at least up to 0.135%. All of the evidence so far acquired on these steels has been derived from bars or rods made on a small laboratory scale, however, and confirmation in large-scale commercial practice, or on steel rolled to sheet form, has not yet been established.

With those limitations understood, this work supports the conclusions of Edwards, Phillips and Jones that the cause of the kind of strain-ageing revealed by the yield-point method, as well as the cause of the yield-point itself, is carbon dissolved in ferrite. Elimination of dissolved oxygen alone apparently has very little effect on that kind of strain-ageing, although oxygen probably is the cause of the kind shown by decrease in impact values.

### The Impact Strength of Ordinary and Special Steels at Sub-Zero Temperatures\*

The ideal curve for the impact strength as a function of temperatures of a pearlitic steel has an S-shape. Curves determined for chromium-nickel-molybdenum and chromium-molybdenum steels, as influenced by heat-treatment, grain size, striking velocity and type of specimens showed highest values at ordinary temperatures and lower values at low temperatures. Chromium-nickel steels gave slightly lower values. Manganese-molybdenum steels, containing manganese 1.42 and molybdenum 0.17%, showed lowest values at ordinary temperatures, but were as good as the chromium-nickel steels at  $-60^{\circ}$  when heat-treated properly.

TABLE X.  
TENSION TESTS OF NORMALISED AND ANNEALED SPECIMENS.

Steel.	Ratio Titanium to Carbon.	Yield Strength (from Fig. 4), psi.	Yield Point by Drop of Beam, psi.	Tensile Strength, psi.	Elongation, %.		Reduction of Area, %
					At Yield Point in 4.5 in.	Total in 6 in.	
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS NOT SUPERHEATED.							
No. 38 . . . . .	0	30,500	30,500	46,300	3.9	32.0	84.3
No. 39 . . . . .	1.0	30,600	31,300	46,800	4.3	31.3	83.0
No. 40 . . . . .	2.2	31,000	31,300	45,800	3.2	32.2	82.6
No. 41 . . . . .	4.4	16,300	—	44,700	0	28.0	89.0
STEELS WITH 0.02 TO 0.045% CARBON, INGOTS SUPERHEATED.							
No. 42 . . . . .	0	30,500	31,000	46,400	3.7	33.7	82.6
No. 43 . . . . .	1.4	24,300	26,600	44,100	3.0	31.3	84.3
No. 44 . . . . .	2.1	26,700	27,300	44,100	2.85	32.3	83.1
No. 45 . . . . .	3.0	15,000	—	45,000	0	32.8	89.4
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS NOT SUPERHEATED.							
No. 46 . . . . .	0.4	45,300	45,100	60,600	4.3	26.7	75.0
No. 47 . . . . .	1.7	41,000	41,600	57,900	4.05	26.7	77.5
No. 48 . . . . .	3.8	44,900	44,900	63,300	3.3	23.3	81.4
No. 49 . . . . .	5.0	21,000	—	54,800	0	20.8	77.8
STEELS WITH 0.12 TO 0.135% CARBON, INGOTS SUPERHEATED.							
No. 50 . . . . .	0	33,000	33,800	52,500	3.4	28.3	73.2
No. 51 . . . . .	0.3	35,400	36,000	59,600	4.25	32.7	75.1
No. 52 . . . . .	1.6	40,500	40,600	57,200	3.35	28.3	77.5
No. 53 . . . . .	3.8	31,500	32,900	55,800	1.25	28.0	84.4
No. 54 . . . . .	5.2	16,700	—	52,500	0	25.8	80.7

\* Adolfo Antonioli, *Atti accad. Italia, Rend. classe sci. fis., mat. nat.*, 2, 361-71 (1941); *Chem. Zentr.*, 1942, I, 2185.

# Gallium : Some of its Properties

By L. Sanderson

*Gallium is among the most scarce of the rare metals; although it is widely distributed in the earth it is only present in small quantities. Its properties are discussed, and brief reference is made to the method of obtaining the pure metal. Its industrial uses are few, but future discoveries may change this position and bring it into line with many other rare metals.*

IT was not until the year 1875 that a French chemist, Lecoq de Boisbaudran, discovered a new metal to which was given the name "Gallium." Boisbaudran was an intelligent man who had theories of his own concerning the spectra of the elements. He had noticed that the spectral lines of the incandescent vapour of the various members of a family of metals are repeated with the same general arrangement, exhibiting regular variations. When he came to the aluminium family of metals, he discovered a peculiar "missing link" lying between indium and aluminium. If such a missing link could be shown to exist, its properties should, he suggested, lie between those of the two metals named. Gaps in the chain of elements are a challenge to the chemist, and the Frenchman began at once, by means of the spectroscope, to try to find the missing metal whose place was vacant. Conditions under which he worked were not exactly favourable, and for five years all his work proved fruitless. In 1868 he amassed a quantity of zinc blende at Pierrefitte in the Pyrenees so as to carry on his inquiries a stage further, but he did not resume work until 1874. Twelve months or so later, on the night of August 27-8, 1875, to be precise, he had the thrill of discovering that the vacant place belonged to a new metal. The name "gallium" was given to it in honour of France, from the Latin name of France—Gallia.

Boisbaudran had, as has been stated, a shrewd notion of what the properties of the new element were likely to be, but he did not attempt to publish his forecasts, preferring to present them to the world as ascertained facts rather than suppositions uncheckered and unproved.

During this period, Mendeléeff was studying the periodic law, and to justify his declaration that a number of gaps in the periodic table could be filled up by unknown elements, he declared that the vacant space below aluminium must belong to an unknown element, to which he gave the name of eka-aluminium. He stated publicly what properties this element should have, and was able to show that gallium possessed them.

Gallium is among the most scarce of the rare metals, although it is widely distributed throughout nature in extremely small quantities. It is a metal of greyish tint, somewhat like steel, with a greenish-blue reflex. On being melted, it presents an appearance indistinguishable from tin or silver. The metal crystallises in bipyramids probably belonging to the monoclinic system or the tetragonal system.

Its specific gravity appears to be in the region of 5.885 when solid and 6.081 in the liquid condition. It is not very malleable. For a time it can be spread under the hammer, but quickly embrittles, fracturing in the direction of the crystalline cleavage on shock or

when suddenly bent. Its compressibility is, when in its state of maximum purity,  $2.09 \times 10^{-6}$  per unit vol. per megabar, at 30° C. The melting point may be taken as 30° C. This means that it may be melted by merely holding it in the hand. The boiling point of the metal is 1,700°. In the molten condition it adheres readily to glass, so that it can be employed to provide mirror surfaces, which are said to be even superior to those of mercury type.

The specific heat is 0.079 between 12° and 23° C. when solid, and between 12.5 and 119° C. in the molten condition it is 0.082. The atomic heat of the solid is 5.52 and for the liquid 5.59. The latent heat of fusion is 18.5 cals. per gram.

Certain chemical properties of the metal should also be noted. It is not affected in lustre by the atmosphere, but is attacked by chlorine, bromine and iodine. It can be dissolved slowly in hydrochloric acid, cold or hot, hydrogen being given off as a result. It goes into solution in nitric acid also, while there are other solvents. It readily forms amalgams with certain metals such as mercury, cadmium, aluminium, platinum, indium, etc. The atomic weight is given by the International Table as 69.9. The atomic number is 31.

It forms two classes of compounds in which it acts as a divalent and trivalent element respectively, but few gallous compounds are known. Gallous oxide appears to form when gallic oxide is reduced in hydrogen at a red heat. Gallous chloride ( $GeCl_3$ ), a white, crystalline, deliquescent solid, exhibits normal vapour density at 1,000° C. Water decomposes it, forming gallic chloride, gallic hydroxide, and hydrogen.

The principal production of the metal was carried on in Germany. No figures are available. The principal use is for dental fillings, quartz thermometers and optical mirrors.

A brief indication of how the metal is obtained in pure form is given. The zinc blende containing the element is treated with insufficient *aqua regia* to effect complete solution, and the solution is then filtered. To this zinc is added to precipitate copper, lead, etc. The clear filtrate from this precipitate is then boiled with excess of zinc. This leads to the precipitation of a highly impure gallic hydroxide, which is dissolved in hydrochloric acid, and the solution saturated with hydrogen sulphide. Any precipitate is filtered off. To the filtrate, ammonium acetate is added, together with some acetic acid, and this liquid precipitated fractionally by hydrogen sulphide until the liquid is freed from gallium when tested by the spectroscope. The precipitate is washed, dissolved in hydrochloric acid, and the gallium again

precipitated as the hydroxide by the zinc method as above.

After some further purification, the oxide is dissolved in potassium hydroxide and the metal obtained by electrolysis. It is deposited at the cathode, and the current density should be much higher at the cathode than at the anode. Platinum electrodes are employed.

Gallium occurs in many zinc blende—e.g., those of Sweden and Saxony, Cumberland and Spain, America, Sardinia and Australia. It is also found in zinc residues after zinc distillation. It is found in about a third of the world's iron ores; in metallic iron; in blast-furnace flue dusts; in aluminium ores; in china clay and bauxite; in commercial alum; in germanite, meteoric iron, and the sun and stars.

Gallic oxide is a white solid formed by heating the nitrate, sulphate or an alum. It is capable of solution in strong acids (unless it has been subjected to intense heat), forming salts, and in alkalis, even ammonia. The hydroxide  $\text{Ga}(\text{OH})_3$  is formed as a white, gelatinous precipitate on adding an alkaline hydroxide to a soluble salt of gallium. It is soluble in excess of alkali, and also in acids, forming gallic salts.

Gallic chloride,  $\text{GaCl}_3$ , is a white, crystalline, hygroscopic solid, with a melting point of  $75.5$  and a boiling point of  $215^\circ$  (approximately). Its vapour density agrees nearly with the formula  $\text{Ga}_2\text{Cl}_6$  at  $273^\circ$ , with  $\text{GaCl}_3$  at  $445^\circ$ . It exhibits slight dissociation about  $1,000^\circ$ . It is highly soluble in water, and the solution undergoes hydrolysis. In short, it bears a great resemblance to aluminium chloride. The sulphate  $\text{Ga}_2(\text{SO}_4)_3$  is highly water soluble. When heated, this solution produces a precipitate of the hydroxide, which redissolves on cooling. It forms alums. The nitrate  $\text{Ga}(\text{NO}_3)_3$  is highly deliquescent.

The ferrocyanide  $\text{Ga}_4(\text{Fe}[\text{CN}]_6)_3$  is important for the reason that it is precipitated from solutions containing gallium in presence of acid. When the salt is heated in air, it gives  $\text{Ga}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .

The potential of gallium lies apparently between indium and zinc, but gallium is distinctly more difficult to precipitate than zinc. It is one of the few elements that expand on solidification, bismuth being another. The cubical coefficient of expansion of the liquid is approximately  $0.000055$  per  $^\circ\text{C}$ , but the metal is incapable of employment in thermometers because it wets glass. Probably the simplest method of separating gallium from indium and zinc is by fractional crystallisation of the caesium alums. The metal cannot be separated by electrolysis of sodium hydroxide solutions in the presence of nitrates.

At the present moment it would be difficult to say that gallium is a metal of primary economic importance. Its industrial uses are relatively few, and its production cannot have attained a high figure. At the same time, the history of the rarer metals is replete with instances of discoveries that have given a new and sustained importance to relatively unknown elements, and it is by no means impossible that gallium at some future date should be put to important use.

The Directors of Vickers, Ltd., advise that an interim dividend of 4% (actual), less income tax, on the Ordinary Stock of the company in respect of the year 1943 will be paid on October 21, 1943.

### Mr. Frank S. Russell

THE death took place at Cheltenham, on September 8, after a long illness, at the age of 65, of Mr. Frank Scott Russell, F.R.S.A., F.G.S., a well-known industrialist. At one time he was chairman of General Refractories, Ltd., manufacturers of refractories. He played a part in the development of a vital war industry—the production of sea-water magnesite. On his removal to Cheltenham from Sheffield he began the Forest of Dean Stone Firms, Ltd.; one of his desires in recent years being to develop the industries of South Wales.

He was chairman of London and Sheffield Publishing Co., Ltd., being the founder, in 1925, of *The Refractories Journal* (the official organ of the Refractories Association of Great Britain), being also instrumental in founding *Claycraft* (the official organ of the National Association of Clayworks' Managers) and *Cement, Lime and Gravel* (which incorporates *The British Limemaster*). He was also chairman of The British Steelmaker, Ltd., and founder of *The British Steelmaker*.

Mr. Russell was born in Hull in 1878, and began his business career with Walker and Hall, Ltd., silversmiths, Sheffield, and later entered the Refractories Industry. In 1913, the General Refractories Co., Ltd. (Mr. Russell being one of the founders) was established. Later this Company was the principal unit in the amalgamation of a number of Companies, and became known as General Refractories, Ltd., with Mr. Russell as chairman.

He was a founder and a past-president of the Refractories Association of Great Britain and also of the National Association of Clayworks' Managers. He was a past-president of the Institute of Quarrying, and connected officially with several other associations.

### The Physical Chemistry of Open-Hearth Slags

(Continued from page 238)

dissociated, so that various amounts of the free oxides also occur. Their method is, however, somewhat "rough," in that they express all slag concentrations as weight percentages, whereas molar fractions are undoubtedly preferable, though adding very considerably to the labour involved in calculating the constants. To compensate for this they fall back in some cases on thermochemical criteria for confirmation.

An entirely different concept of slag constitution has been put forward by Herasymenko,<sup>12</sup> who believes that the slag compounds undergo complete dissociation of an ionic type in the liquid slag in the same manner as do most salts on melting.<sup>†</sup> McCance,<sup>13</sup> on the other hand, has suggested that the variations observed in the values of the slag-metal constants may be due mainly to changes in the activity coefficients of the reactants brought about by changes in slag composition. The methods described above depend on the assumption that such influences are of secondary importance only. In view of the magnitude of the composition changes involved, this would appear rather a considerable assumption to make, and its final justification will depend entirely on the extent to which methods of this kind can interpret the behaviour of the liquid slag.

<sup>12</sup> Herasymenko, *Transactions of the Faraday Society*, 1938, vol. 34, p. 1,245.

<sup>13</sup> McCance, "The Application of Physical Chemistry to Steelmaking," *The Iron and Steel Institute*, 1938, Special Report No. 22, p. 331.

<sup>†</sup> As molten slags appear to have appreciable electrical conductivity it is probable that some dissociation of this type does occur.

# Direct Cooling Process for Casting Aluminium Alloy Ingots

By A Special Correspondent

*A noteworthy advance in the perfection of a process for direct cooling of ingots and billets, whilst they are being poured, is discussed. Although concerned primarily with aluminium alloys, it is suggested that the process may also be advantageous with bronzes and other non-ferrous alloys.*

SINCE 1910, when Wilm developed the now world-famous wrought alloy, Duralumin, and discovered the age-hardening phenomenon, which had far-reaching effects and gave fresh impetus to the aluminium industry, progress has not been concerned with the discovery of new alloys, but rather with improvements of existing alloys and the various methods of processing them. Thus, the well-known Y-alloy, for high-temperature applications, and the Hiduminium range of alloys, may be regarded as typical examples of alloy developments in Britain which followed those of Wilm. Parallel with alloy developments, however, great strides were made in manufacturing technique. Sand-, die-, and ingot-casting processes have now become highly developed, while on the wrought side, pressing, extrusion, tube-drawing, and rolling of sheet and strip have been added to the older forging and stamping processes of working high-strength aluminium alloys.

A more recent noteworthy advance in processing concerns the perfection of a process for the direct cooling of ingots or billets with water whilst they are being poured. This is a development by the Vereinigte Leichtmetall-Werke, of Hanover, which is described in British Patent Specifications No. 492,216. In the process developed the metal is poured into a short water-cooled mould from which the bottom is lowered at such a rate that the ingot is not completely solid when it leaves the mould, thus permitting cooling water to come into direct contact with the ingot metal almost immediately after casting.

For casting aluminium containing 3.5 to 4.5% of copper and 0.6 to 1.4% of both magnesium and manganese, an example is cited in which a mould may be 25-30 cms. in diameter and 16-20 cms. long, into which the metal is poured to within 4 to 5 cms. of the top and the ingot lowered at the rate of 50-90 cms. per min. Several methods of cooling the mould and the ingot are given in the specification.

Many investigators, particularly in Germany and the U.S.A., have experimented with devices designed to accelerate the rate of freezing non-ferrous ingots when being cast. This is of particular importance in the case of aluminium alloys, where the resultant relative freedom from segregation of alloying constituents and fine grain structure are of extreme importance, since they govern the properties of any wrought materials subsequently produced from the cast ingots or billets.

Several means of chilling ingots have been devised, and they include the employment of copper moulds, water-cooled iron moulds and moulds made of light steel sheet which are submerged in water either before or immediately after casting.

It was in Germany that a method of applying the coolant directly to the ingot being cast was first investigated, and in the early stages of the experimental work the great advantage of having continuous contact between the cooling water and the ingot was emphasised, since this solved the problem associated with the contraction of the freezing metal away from the surface of any mould, and thereby providing an insulating layer of air between the mould surface and the ingot. The remarkable improvement in the metallurgical structure of the ingots produced by direct cooling prompted the V.L.W. to carry out more thorough and exhaustive experiments, with the result that they arrived at a means whereby, to use the terms of the Patent Specification mentioned above, "the molten metal is poured into a short water-cooled mould, the bottom of which is lowered meanwhile at such a rate in relation to the rate of pouring that the level of the molten metal remains more or less constant, where the rate of pouring is of such magnitude compared with the size of the mould that the ingot has not yet completely solidified through to the centre when it leaves the bottom of the mould, this (complete solidification) only taking place subsequently by direct contact with the cooling liquid." Since there is no fixed bottom to the mould provision can be made for pouring to continue as long as required. For this reason this method of casting is sometimes described as the "continuous casting process."

After a number of trials it was found that the mould could be shortened very considerably and the chief novelty described in the Patent Specification under reference is that the mould is shorter in vertical height than the smallest diameter of the ingot, billet or slab being cast.

At first it was thought that the shortening of the mould might result in a very considerable slowing up of the rate of pouring, if the solidified walls of the ingot were to be sufficiently strong to contain the molten interior metal, but in practice it was found that cylindrical billets of over 40 centimetres diameter could be cast at speeds of up to 15 to 20 centimetres per min. provided that adequate supply of cooling water at approximately normal temperature were provided. In this connection British Provisional Patent Specification No. 61177 describing results of investigation by Appleby is interesting in that it describes a particular and improved type of water injection on to the ingot which is designed to produce the optimum rate of heat transfer to the coolant.

It seems probable that the importance of the direct cooling process has not been sufficiently appreciated in this country since many manufacturers, so far, have

failed to avail themselves of the many advantages accruing from it; one of the latter is that the much improved properties obtained in some Duralumin types of alloy sheet, rolled from directly cooled slabs, permit of the specification mechanical properties being obtained whilst using much lower magnesium content than would be required when employing slabs cast in ordinary chill moulds. This, of course, gives much better rolling characteristics. Similar improvements in properties are

obtained in extruded sections or forgings made from directly cooled billets.

Although there is no record of serious investigation, having been carried out in this country, it is probable that, by using this process, improvements comparable with those mentioned above might be obtained with bronzes and other non-ferrous alloys, but certainly the results so far obtained appear to warrant the closest attention of all metallurgists engaged in experimental or research work in connection with non-ferrous metals.

## Reviews of Current Literature

### The Metallurgy of Deep-Drawing and Pressing

ORIGINALLY published in 1940, the fact that there was a demand for a second edition within six months is very significant. It certainly shows that great was the need for a reliable and authoritative book on a subject which has become so important in recent years. It is doubtful whether any single process contributes more to the rapid production of both ferrous and non-ferrous metal parts as deep-drawing and pressing. Developments and improvements in the process have, in many respects revolutionised the manufacture of countless products and has enabled them to be produced at a speed which has greatly reduced their cost.

The author deals with the subject in a comprehensive way; not only does he deal with pressing operations in an authoritative manner, but the book embraces information covering the manufacture of deep-drawing materials, methods of testing, defects and difficulties encountered in materials used for pressing. In addition presses, tools and lubricants are specially considered. In preparing the present edition the author has taken the opportunity to make such additions and modifications as new work published too late to be assessed in the first edition has rendered desirable, and also to enlarge the section dealing with light alloys and with "soft metal" tools.

This book of 740 pages will be invaluable to all engaged in deep-drawing and pressing work, whether on the practical or scientific side, and it can be regarded as a standard work on the subject, one which will be used for reference purposes for many years to come. It is admirably produced and well illustrated; an interesting feature being the half-tone illustrations, of which there are a considerable number, and are printed on cream art paper.

By J. Dudley Jevons, Ph.D., B.Sc., A.I.C., with a Foreword by H. W. Swift, M.A., D.Sc.; published by Chapman and Hall, Ltd., 11, Henrietta Street, London, W.C. 2. Price 60s. net.

### Fusion Welding of Wrought-Aluminium Alloys

ALTHOUGH aluminium has been welded successfully for some forty years, there are still many in industry who are not familiar with the technique required for fusion welding of aluminium, whilst even less is known about the welding of the alloys. The problems to be overcome are due to the characteristics of the metal, and these problems have

been solved by changing the practice established for other materials having different properties. The practice adopted for aluminium and its alloys is admirably described in a booklet recently published by the Wrought Light Alloy Development Association.

It deals first with the underlying reasons for the various difficulties encountered by operators inexperienced in the welding of aluminium. For example, the reasons for the difficulty of seeing exactly when fusion takes place, and the necessity for using flux mixtures of a certain type are explained. It also describes how the characteristics of the metal affect the welding procedure required for each of the fusion processes. A table is included summarising processes recommended for each type of aluminium alloy.

In addition to full descriptions of the oxy-acetylene and other oxy-gas methods, details are given of the metallic arc process, as well as several other processes not hitherto described in publications of this nature, such as the Weibel and Technotherm methods.

The booklet is very fully illustrated with both photographs and diagrams, particularly on those pages devoted to the preparation of the work, and the various welding techniques—leftwards, vertical upwards, etc. Flux compositions are summarised, and the methods of finishing, including removal of flux residues, are detailed.

Seven tables summarise basic data, such as gas consumption, electrode size and current requirements, and even the information required for estimating welding costs. There is also a short section on the inspection of fusion welds, with diagrams giving added point to the text.

This information is contained in W.L.A.D.A. Bulletin No. 5, and copies are available to all responsible persons with an interest in the welding of wrought-aluminium alloys on application to the Association, Unwin Chambers, 62, Temple Row, Birmingham, 2.

### Director of Light Metals (Extrusions) Control

Mr. HORACE W. CLARKE retired from the directorship of the Light Metals Extrusions Control, for the organisation of which he was initially responsible in October, 1939. He is succeeded by Mr. G. Meredith, previously deputy-director under Mr. Clarke. Mr. H. J. Sells becomes deputy-director, and Mr. W. H. Smith, assistant director.

Mr. Clarke is managing director of James Booth and Sons, Ltd., and of Wilkes, Sons and Maplebeck, Ltd. He has been chairman of the Wrought Light Alloys Association since its inception, and is actively concerned with other non-ferrous metal trades associations, as well as being a member of the Grand Council of the F.B.I.

## A Welding Flux for Monel Metal

By W. M. Halliday

THE stainless group of alloy steels, and especially Monel metal, present their own peculiar problems and obstacles in the way of successful welding for the welding engineer, and the reaction and behaviour of ordinary fluxes employed on other more common metals does not always follow the lines expected, or give results which are satisfactory. It has, of course, been claimed that good welding of such metals can be accomplished without the use of a flux at all, providing certain careful steps are taken to obviate all oxidation, and scaling. Unfortunately, with most workshop plants of customary type oxy-acetylene machines or equipment the task of totally excluding oxidation tendencies is not always feasible or successful, and in any case much trouble and added expense is likely to arise from any efforts made in such directions, unless a flux is employed.

One of the chief reasons, but not the sole one, of course, for the use of a flux is to assist in arresting the oxidation of the surfaces to be welded which arises when heated up, and in some materials proceeds at a very rapid rate indeed. Thus, a good economical fluxing mixture which will assist both in preventing oxidation, scale formation, and at the same time promote the flow of welding metal, will, in practice, be found most advantageous and valuable, and certainly well worth the little trouble needed for its manufacture and application.

It is to be regretted that apparently the study of the behaviour, applications and properties of fluxes employable in connection with stainless steels in general, and Monel metal in particular has been somewhat neglected. The reasons perhaps for this lack of scientific investigation may be due to the fact that there is a growing tendency to conduct welding operations without flux at all wherever it is at all possible. Thus, the use of fluxes tends to be discouraged, and less thought and consideration is therefore applied to their value and capacities.

To weld Monel metal by the oxy-acetylene method, a very useful time-saving flux to employ can be made up from the following recipe which has been used by a practical welder with excellent results. The constituents of this flux are as follows: Borax, in either crystal or flour powder form; boric acid, in crystal form; boric acid, in crystal form; sodium silicate (this, of course, is ordinary water-glass); distilled water. Borax in crystal form will be found the most suitable.

First, equal parts of borax and boric acid are dissolved completely in hot distilled water. One pint of water per 6 oz. each of boric acid and borax will be found a useful and convenient consistency. The resulting mixture then should be combined in equal parts with diluted sodium silicate, this latter having previously been reduced to approximately two-thirds its original strength by application of distilled water.

Ordinary water may, of course, be used, but distilled water has been found far more reliable, due to the fact that its use avoids numerous sources of contamination of the resulting flux. Trouble with finished flux when ordinary undistilled water had been used were traceable to the presence of innumerable micro-organisms in the water, setting up decomposition in the sodium silicate.

The mixture should be made up in the form of a

thickish creamy paste, stiff enough to adhere snugly to a surface of component to be welded, whether in an angular or vertical position.

The flux can be kept for a long period providing it is carefully stored in an air-tight container, and, of course, kept free from dirt, dust or excessive moisture.

In applying the flux a brush should be employed and the surfaces well cleaned before coating. All the seams and joints which are to be welded should be completely covered by flux just prior to heating up so as to exclude the surface from all contact with external air. If this is done oxidation will be reduced to a minimum and a satisfactory weld made which, incidentally, should possess a far smoother surface and better appearance than is usually the case with such operations.

### A New Bimetal Battery Can

In battery manufacture it is recognised that to cover the zinc can with an external layer of lead will render the can immune to attack by the electrolyte and thereby preserve the usefulness of the cell, even in the case of local perforations of the zinc sheet. The idea of using such an expedient is accepted as being fundamentally sound. Until recently, however, technical difficulties have prevented the commercial application of this idea. The main difficulty encountered has been the production of lead-coated cans possessing a lead coat of sufficient thickness which could be manufactured at a low cost. This problem has now been solved in a novel way which presents no manufacturing difficulties, and incidentally effects considerable economy in zinc.

Present battery cans, whether made by drawing, impact extrusion, or soldering of flat sheet, have to be of a thickness of at least 0.01 in. in order to enable the forming into a can, as well as to protect against premature perforation. The fact, however, that only a mere fraction of the zinc is actually consumed in the total lifetime of the cell and the remainder is lost means a very considerable wastage. This new can is made of two sheets of metal foil, an external one of lead and an internal one of zinc, formed into cup shape by folding along a multitude of radial folds compressed into a substantially smooth surface with the two portions securely interlocked along the pleats. By this method there is no limit to the thinness of the metal sheets employed, and the thickness of the zinc sheet can be almost exactly adapted to the actual consumption of zinc in the creation of electrical energy and the local action.

The quantity of zinc is, therefore, only a fraction of that which is now required in a battery can, and even the combined amount of zinc and lead is substantially below the usual. Perforation of the zinc at one or several points does not affect the further function of the cell, due to the protective lead cover. No seepage of electrolyte can take place and the cell remains useful until practically all the zinc has been consumed.

By giving the cans a slightly conical shape they can be nested into one another. In this state they protect each other from damage in transit and only occupy a fraction of the space required for cylindrical cans. For use in high-tension batteries the connection wire can be affixed to the can by clamping in between the zinc and the lead with or without the aid of solder.

This new battery can, known as the "O.J.B. bimetallic battery can," is manufactured by Andersen and Bruun (British), Ltd., Edinburgh Avenue, Slough.

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